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**APPLICATION NUMBER: 60/636,565**

**FILING DATE: *December 16, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US05/05574***



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15866 U.S. PTO

121604

PTO/SB/16(10-01)

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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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121604

INVENTOR(S)		
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
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<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto		
TITLE OF THE INVENTION (500 characters max)		
NON-POROUS ADHERENT INERT COATINGS AND METHODS OF MAKING		
Direct all correspondence to:		
<input checked="" type="checkbox"/> Customer Number 21269		
Place Customer Number Bar Code Label here		
OR		
<input type="checkbox"/> Firm or Individual Name		
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City	State	ZIP
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ENCLOSED APPLICATION PARTS (check all that apply)		
<input checked="" type="checkbox"/> Specification	Number of Pages 56	<input type="checkbox"/> CD(s), Number
<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets 7	<input checked="" type="checkbox"/> Other (specify) Postcard, Certificate of Mailing
<input checked="" type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT		
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		
FILING FEE AMOUNT (\$) 100.00		
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees		
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 50-0436		
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.		
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.		
<input checked="" type="checkbox"/> No.		
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____		

Respectfully submitted

SIGNATURE

TYPED or PRINTED NAME Raymond A. MillerTELEPHONE 412-454-5000

Date December 16, 2004,

REGISTRATION NO. 412,891

(if appropriate)

Docket Number: 126457.01210

**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

15866  
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U.S. PTO

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Approved for use through 07/31/2006. OMB 0651-0032

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Effective on 12/08/2004.

Fees pursuant to the Consolidated Appropriations Act, 2005 (H.R. 4818).

# FEE TRANSMITTAL

## For FY 2005

☒ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT (\$)

### Complete if Known

Application Number	Not yet assigned
Filing Date	December 16, 2004
First Named Inventor	Wargo
Examiner Name	Not yet assigned
Art Unit	Not yet assigned
Attorney Docket No.	126457.01210

### METHOD OF PAYMENT (check all that apply)

☒ Check ☐ Credit Card ☐ Money Order ☐ None ☐ Other (please identify): \_\_\_\_\_

☒ Deposit Account Deposit Account Number: 50-0436 Deposit Account Name: Pepper Hamilton LLP

For the above-identified deposit account, the Director is hereby authorized to: (check all that apply)

☐ Charge fee(s) indicated below ☐ Charge fee(s) indicated below, except for the filing fee

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### FEE CALCULATION

#### 1. BASIC FILING, SEARCH, AND EXAMINATION FEES

Application Type	FILING FEES		SEARCH FEES		EXAMINATION FEES		Fees Paid (\$)
	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	Fee (\$)	Small Entity Fee (\$)	
Utility	300	150	500	250	200	100	
Design	200	100	100	50	130	65	
Plant	200	100	300	150	160	80	
Reissue	300	150	500	250	600	300	
Provisional	200	100	0	0	0	0	100.00

#### 2. EXCESS CLAIM FEES

Fee Description	Fee (\$)	Small Entity Fee (\$)
Each claim over 20 (including Reissues)	50	25
Each independent claim over 3 (including Reissues)	200	100
Multiple dependent claims	360	180
<b>Total Claims</b>	<b>Extra Claims</b>	<b>Fee (\$)</b>
- 20 or HP = _____ x _____ = _____		
HP = highest number of total claims paid for, if greater than 20.		
<b>Indep. Claims</b>	<b>Extra Claims</b>	<b>Fee (\$)</b>
- 3 or HP = _____ x _____ = _____		
HP = highest number of independent claims paid for, if greater than 3.		

#### 3. APPLICATION SIZE FEE

If the specification and drawings exceed 100 sheets of paper (excluding electronically filed sequence or computer listings under 37 CFR 1.52(e)), the application size fee due is \$250 (\$125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

Total Sheets \_\_\_\_\_ Extra Sheets \_\_\_\_\_ Number of each additional 50 or fraction thereof \_\_\_\_\_ Fee (\$)  
\_\_\_\_\_ - 100 = \_\_\_\_\_ / 50 = \_\_\_\_\_ (round up to a whole number) x \_\_\_\_\_ = \_\_\_\_\_ Fee Paid (\$)

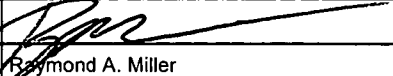
#### 4. OTHER FEE(S)

Non-English Specification, \$130 fee (no small entity discount)

Other (e.g., late filing surcharge): \_\_\_\_\_

Fees Paid (\$)

#### SUBMITTED BY

Signature		Registration No. (Attorney/Agent) 42,891	Telephone 412-454-5000
Name (Print/Type)	Raymond A. Miller		Date December 16, 2004

This collection of information is required by 37 CFR 1.136. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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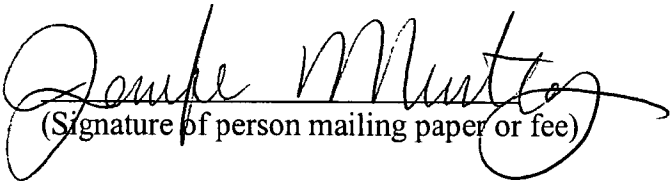
**CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.10**

APPLICANTS: WARGO et al.  
TITLE: NON-POROUS ADHERENT INERT COATINGS AND  
METHODS OF MAKING  
SERIAL NO.: NOT YET ASSIGNED  
ATTORNEY REF: 126457.01210  
DATE OF DEPOSIT: DECEMBER 16, 2004  
EXPRESS MAIL NO. EV472064845US

I HEREBY CERTIFY THAT THIS PROVISIONAL PATENT APPLICATION IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE VIA UNITED STATES POST OFFICE EXPRESS MAIL UNDER ON THE DATE INDICATED ABOVE AND IS ADDRESSED TO THE COMMISSIONER FOR PATENTS, P.O. BOX 1450, ALEXANDRIA, VA 22313-1450.

Jennifer Martinez

(Typed or printed name of person mailing paper or fee)

  
(Signature of person mailing paper or fee)

Documents sent:

- ☒ Provisional Cover Sheet
- ☒ Application (56 pages)
- ☒ Formal Drawings (7 sheets)
- ☒ Applicant Data Sheet
- ☒ Fee Transmittal & Check in the amount of \$160
- ☒ Certificate of Mailing

## **NON-POROUS ADHERENT INERT COATINGS AND METHODS OF MAKING**

### **CROSS REFERENCE TO RELATED APPLICATIONS**

**[0001]** This application incorporates by reference in its entirety U.S. Provisional Application Serial Number 60/546,680 filed February 20, 2004.

### **BACKGROUND AND SUMMARY**

**[0002]** There is a continuous effort to develop pressure sensors, chemical sensors, and housing materials that are lower in cost and smaller in size, yet are characterized by high reliability, sensitivity, and linearity. For example, multiple pressure sensors, temperature, and optical sensors having sensing diaphragms, cavities, and resistive elements can be made on a single silicon wafer using semiconductor fabrication processes. In the processing of such cells, sensor elements such as the thin diaphragm of a pressure sensor are formed in a silicon wafer through preferential chemical etching. Ion implantation and diffusion techniques are then used to drive doping elements into the diaphragm, forming resistive bridge circuit elements whose electrical resistance changes with strain. As a result, deflection of the diaphragm causes a change in resistance value of the piezoresistive elements, which can then be correlated to the magnitude of the pressure applied to the diaphragm.

**[0003]** The use of standard single-crystal silicon wafers and standard semiconductor device fabrication processes allows many such cells to be fabricated from a single wafer, providing some economy of scale. However, silicon is susceptible to chemical attack, particle generation, and erosion by various media, particularly in applications where a high-pressure, temperature, and corrosive fluids are to be sensed, e.g., semiconductor manufacturing, long term

medical implants, and automotive applications. One particularly difficult and sensitive application of integrated circuits, semiconductors and metal electrodes is in electrical or electronic device implantation in a human or animal body. Extra-cellular fluids within the body are saline, and often contain a number of other ions or other electrolytes. At body temperatures, severe and rapid corrosion may lead to rapid and untimely failure of the device. For such applications, a pressure, temperature, or chemical sensor and fluid handling devices in contact with these fluids (i.e. catheters, pumps, heat exchangers, or conduits) must also be of high chemical purity, physically rugged and resistant to the hostile environment of the sensed medium. It would be advantageous that a micromachined silicon sensor cell include some form of protection in order to realize its superior operational characteristics in the chemically hostile environment. Current methods for producing media-compatible, high-pressure sensors include enclosing a silicon sensing chip in an inert fluid, such as a silicone oil or gel, and then further separating the sensing chip from the medium to be sensed with a metal diaphragm, such that pressure must be transmitted through the metal diaphragm and fluid to the sensing chip. While achieving some of the operational advantages of silicon pressure transducer cells, the manufacturing processes for these sensors are relatively expensive and complicated.

**[0004]** Piezoelectric and capacitive pressure sensors are typically thin ceramic plates or diaphragms that may be coated with thick-film electrodes or bridge elements to form capacitors or strain sensing elements. However, each of these also have certain disadvantages, such as complex circuitry to detect capacitance changes, the requirement for ceramic-to-ceramic bonds, and a maximum pressure capability typically not exceeding about 1000 psi (about 7 MPa). For higher pressures, metal diaphragms have found use as the sensing element, however these diaphragms are not generally useful in corrosive aqueous solutions. Metal diaphragms generally

deflect more for a given thickness and pressure than ceramic diaphragms. With metal diaphragms bridge elements or electrodes may be deposited on to a dielectric insulating layer on the metal followed by thin-film polysilicon or metal deposited on the metal diaphragm to form the bridge or electrode structures. For example, a thin-film polysilicon layer is deposited on the dielectric to form the piezoresistors of the bridge, followed by thin-film metallization to provide electrical interconnects. As is conventional, the thin-film layers are typically deposited by such processes as chemical or physical vapor deposition. The equipment necessary for these processes is expensive, and deposition rates are extremely slow and difficult to use with complex structures and large structures like housings, bellows, or conduits. Deposition of the thin-film layers requires multiple patterning, exposure, developing and stripping steps for the required thin-film photoresists and metallization, and must be carried out in a controlled environment to assure that no air borne particles are present on the surface to be coated. In addition, because such processes deposit thin-films usually no thicker than 10,000 angstroms, the surface of the metal diaphragm must be extremely smooth to avoid rough surface features penetrating through or producing discontinuities in the deposited thin films. Finally, the resistance of the resulting polysilicon thin-film piezoresistors can vary dramatically with temperature.

**[0005]** Typically, a sensor is contained within a chemically and mechanically protective housing. The housing essentially surrounds the sensor and any associated electronics for sensor excitation and signal processing. While this provides mechanical protection for the sensor, protection from hazardous chemicals and contaminants in the medium must also be provided. In one type of pressure sensor assembly, a silicone gel, fluorosilicone gel, or silicone oil is applied over the external surface of a pressure sensor and essentially partially fills the housing in which



the pressure sensor is mounted. The gel or oil is covered with a membrane. The manufacture of these cells can be cumbersome and expensive.

[0006] Various materials have been developed to provide an electrically insulative moisture barrier over a substrate. Among the more prominent of these are aromatic polyimides such as those sold under the trade designation "Kevlar" by E.I. DuPont de Nemours, & Co. However, polyimides are highly viscous, difficult to deposit, and can easily entrain gas bubbles leading to film defects. Parylene N coatings are produced by vaporizing a di(p-xylylene) dimer, pyrolyzing the vapor to produce p-xylylene free radicals, and condensing a poly-oligomer from the vapor onto a substrate that is maintained at a relatively low temperature, typically ambient or below ambient. Parylene N is derived from di(p-xylylene), while parylene C is derived from di(monochloro-p-xylylene), and parylene D is derived from di(dichloro-p-xylylene).

[0007] Although parylenes have generally advantageous electrical, chemical resistance and moisture barrier properties, it has been found that these poly-oligomers do not adhere well to many substrate surfaces, particularly under wet conditions. Although these poly-oligomers are quite resistant to liquid water under most conditions, they are subject to penetration by water vapor which may condense at the interface between the parylene film and the substrate, forming liquid water which tends to delaminate the film from the substrate. Vapor deposited parylene films are also generally quite crystalline and are subject to cracking which may also create paths for penetration of moisture to the substrate surface. Parylene has been used to protect devices and larger substrates, or a thermally bonded fluorinated polymer casing has been used. Both have been found to offer relatively poor performance in critical applications. The parylene coatings suffer from high diffusion rates, and the thermally bonded devices, provided the devices

or substrate can tolerate the processing conditions, have been known to undergo mechanical stress cracking at the bond seams.

**[0008]** These organic coatings may be used either alone or together with fluorosilicone gels. Fluorosilicone gels are used to protect the sensor device, wirebonds, portions of the package, and leads. Fluorosilicone gels have several disadvantages including an incompatibility with fuels (e.g., swelling).

**[0009]** This invention relates to protective coatings on sensor substrates, and optical substrates, housings, or fluid handling substrates and more particularly to a novel process for providing a tough, adherent, insulating coating that constitutes a barrier against penetration of fluids and ions to the surface of the sensor, electrodes, other structure deposited on the sensor, housing surfaces, or other structures in contact with fluids like impellers, bellows, and mixers.

**[0010]** Embodiments of the present invention include a structures having an effective thickness of a protective non-porous coating that is adherent and chemically bonded to a surface of the structure in contact with a fluid. Structures coated may be but not limited to a sensor, a conduit, a vessel such as a cuvette or gas sampling cell, bellows, surface of fluid handling equipment, or transparent windows that are to be contacted with a fluid during chemical processing and preferably a fluid whose properties are to be measured, characterized, or transported. The protective and adherent coating is chemically inert, has low permeability to fluids, ions and gases. The adherent non-porous coating on a surface of the structure reduce or protect it and structures formed on such as electrodes and electrical structures from corrosion, particle generation, delamination, swelling. The coating on the surface of the structure can reduce or prevent changes in response, sensitivity, or performance caused by the adverse effects of the fluid in contact with the underlying substrate. The coating is prepared from a coating

material that includes a solvent and a poly-oligomer or poly-oligomer that contains fluorine and reactive groups for chemically bonding a portion of the poly-oligomer to the sensor surface. The adherent coating can be formed by evaporation of solvent from a bubble free volume of coating material deposited onto the sensor surface to form a non-porous film. The non-porous film is cured to form the protective non-porous coating; the coating adheres to the substrate surface and at least a portion is chemically bonded to the surface of the sensor. The curing preferably occurs at a temperature that does not adversely affect the underlying substrate and can be less than the boiling point of the coating material solvent(s) and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. The cured film having a density, thickness and mass which permits the substrate or sensor to function in a device or produce a measurable physical response to energy input. The coating protects or reduces the effects of corrosive fluids to the underlying substrate or to the sensing device and protects them from particle generation, degradation, swelling, or corrosion especially in high purity corrosive fluids.

[0011] Embodiments of the present invention include fluid contacting structures having an effective thickness of a protective non-porous coating that is adherent and chemically bonded to a surface of the structure in contact with a fluid. The non-porous coating protects the underlying structures from corrosion, swelling, particle generation, delamination, or generation of contamination. Structures coated with the non-porous adherent coating in contact with a fluid may include but are not limited to sensors, conduits, a vessel such as a cuvette, pump housings, mixers, stirrers, impellers, gas sampling cell, bellows, material handling equipment like pumps, flow meters, or flow controllers or transparent windows that are to be contacted with a fluid

during chemical processing. The housing may be made of a chemically suitable material, preferably a material which is chemically inert to the fluid. Some housing materials may include a coating of the poly-oligomeric material applied to a portion or all of the housing surfaces. The protective and adherent coating is chemically inert, has low permeability to fluids, ions and gases. The adherent non-porous coating on various substrate surfaces protect the substrate from corrosion, particle generation, delamination, or chemical and or physical changes caused by the fluid. The coating is prepared from a coating material that includes a solvent and a poly-oligomer or poly-oligomer that contains fluorine and reactive groups for chemically bonding a portion of the poly-oligomer to the substrate surface. The adherent coating can be formed by evaporation of solvent from a bubble free volume of coating material deposited onto the substrate surface to form a non-porous film. The non-porous film can be cured to form the protective non-porous coating; the coating adheres to the substrate surface and at least a portion is chemically bonded to the surface of the substrate. The curing preferably occurs at a temperature less than the boiling point of the coating material solvent(s) and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the substrate. The cured film having a density, thickness and mass which permits the substrate to operate or function in a material or fluid handling device. The non-porous adherent coating protects that portion of the material handling from particle generation, degradation, and corrosion especially in high purity corrosive fluids, and materials such as slurries.

[0012] One embodiment of the present invention is a sensor having a surface with an effective thickness of an adherent protective coating on the surface of the sensor for contacting a

fluid to be measured. The property of the fluid to be measured may include but is not limited to pressure, flow, temperature, chemical composition, chemical purity, or a combination of these. The coating preferably results in an adherent non-porous coating on a surface of the sensor which protect it and structures formed on it from corrosion, particle generation, delamination, or changes in sensor response and sensitivity caused by the fluid. The coating includes a soluble poly-oligomer containing fluorine, that is chemically bonded to the sensor surface to form an adherent protective coating. The adherent coating is formed by curing a non-porous evaporated film of the coating material formed or placed on the surface of the sensor. Preferably the curing occurs at a temperature less than the boiling point of the coating material solvent and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. The device and sensor may include structures for probing by electrical energy, light energy, mechanical energy, or chemical interaction the state of the sensor and means or structures for measuring said physical response of said sensor to the excitation. Such structure on one or more of its surfaces may include but are not limited to resistive, capacitive, transistors, electrical contacts, optical contacts, or a combination of these. The sensor includes a ceramic material. Preferably the non-porous film of the coating material formed or placed on the surface of the sensor includes greater than 10% of the poly-oligomer in the coating material deposited on the substrate to form the non-porous film. The sensor may be used to measure one or more fluid properties such as but not limited to temperature, flow, chemical purity, pressure, or a combination of these. The poly-oligomer coating material deposited or applied to the sensor surface can include an organosilane adhesion promoter. The adherent protective coating can be

formed on one or more surfaces of the sensor. Preferably the adherent protective coating is at least 50 micron thick. The sensor surface can be treated to chemically bond the poly-oligomer to the sensor surface. The poly-oligomer may bond to surface groups that includes but are not limited to reactive amine, hydroxyl, carboxylic, ester, amide, or thiol groups for bonding the fluorine comprising poly-oligomer to the sensor surface.

**[0013]** Another embodiment of the present invention is a method for measuring a fluid property such as pressure, flow, temperature, chemical composition, chemical purity, or a combination of these in for example a fluid sample or fluid in a conduit. The method includes contacting fluid with a sensor having a surface with an effective thickness of an adherent protective coating on the surface of the sensor for contacting the fluid to be measured. The adherent coating including a soluble poly-oligomer containing fluorine where a portion of the poly-oligomer is chemically bonded to the sensor surface to form an adherent protective coating. The adherent coating is formed by curing a non-porous film of the coating material formed or placed on the surface of the sensor. Preferably curing occurs at a temperature less than the boiling point of the coating material solvent and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. Applying energy to the adherent coated sensing device, measuring the physical response of the sensor, and comparing the physical response to a standard relationship allows correlation of the coated sensor's physical response to a property of the fluid such as but not limited to pressure, temperature, purity, flow or a combination of these. The method can be performed using coated a sensor that is a piezoresistive, piezoelectric, or thermoresistive material. The method may be performed using a coated sensor that includes one

or more plates in capacitive sensor, having two plates and the adherent non porous perfluorinated coating is positioned on one of said plates on a surface in contact the fluid.

[0014] Another embodiment of the present invention is a method of making a coated sensor that includes forming a non-porous film of a coating material deposited on a chemically bondable fluid contacting surface of a sensor. The non-porous film of coating material includes a soluble poly-oligomer containing fluorine and reactive groups on the poly-oligomer. At least a portion of the poly-oligomer reactive groups are chemically reacted with groups on the surface of the sensor for bonding at least a portion of the poly-oligomer to the chemically bondable fluid contacting surface of the sensor. The non-porous film on the chemically bondable fluid contacting surface of the sensor includes greater than 10% of the poly-oligomer deposited to form the non-porous film, and preferably little or no coating material is wasted. The non-porous film may be formed by evaporation of the solvent from the coating material deposited on the sensor, alternatively a film of non-porous material may be placed on the sensor surface. The non-porous film of the coating material is cured on the chemically bondable fluid contacting surface of a sensor with the curing chemically bonding the poly-oligomer reactive groups to the chemically bondable surface of the sensor surface to form an adherent protective coating on the surface of the sensor. The non-porous film of the coating material on the chemically bondable fluid contacting surface of the sensor is formed by removing solvent from a solution of the poly-oligomer contacting surface of the sensor. The curing step preferably occurs at a temperature below which damage to resistive structures, capacitors, transistors, electrical contacts, optical contacts, or a combination of these results. Preferably curing occurs at a temperature less than the boiling point of the coating material solvent and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater

than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. Even more preferably the curing is at a temperature of less than about 120°C. The method may be performed where the fluorine containing poly-oligomer includes an aliphatic ether ring in the chain of the poly-oligomer. In the method the fluid contacting surface can be cleaned and made chemically bondable by a treatment chosen such as but not limited to plasma etching, chemical modification with an adhesion promoter, oxidation, or hydroxylation of a surface. The sensor used in the method may include on one or more of its surfaces structures such as but not limited to resistor bridges, resistors, capacitors, electrodes, transistors, electrical contacts, optical contacts, bonding pads or a combination of these. The coating material may include an organosilane adhesion promoter to react with the sensor surface and also the reactive groups in the poly-oligomer to bond at least a portion of the poly-oligomers to the sensor surface to form an adherent protective film on the sensor surface. The method may be used to form an adherent protective coating on the surface of the sensor has a thickness of greater than 50 microns, greater than 100 microns, greater than 2,500 microns and multiple coatings may be deposited and cured. The method of coating may be used to coat a sensor diaphragm. The method may have the sensing means or structures such as but not limited to electrodes, resistive bridge structures, thermistors, optical and electrical input and output connection formed on a surface of the sensor prior to coating and prior to curing with the coating material. The method may involve solvent removal from coating material applied to the sensor surface to form the non-porous film where the evaporation is performed in an antistatic environment. The method may use curing that can be but is not limited to chemical curing, thermal curing, photochemical curing or a combination of these.



[0015] Another embodiment of the present invention is a sensing device for measuring the property of a fluid such as but not limited to pressure, flow, chemical purity, chemical composition, or a combination of these. The device includes a sensor having a surface with an effective thickness of an adherent protective coating on a surface of the sensor that is used for contacting a fluid to be measured. The coating includes a soluble poly-oligomer containing fluorine, where at least a portion of the poly-oligomer is chemically bonded to the sensor surface to form an adherent protective coating. The adherent coating can be formed by curing a non-porous evaporated film of the coating material formed or applied on the fluid contacting surface of the sensor. The device includes structures or means for applying energy to sensing device for excitation and means or structures for measuring the physical response of the sensor to the excitation and the fluid. The device includes a housing which isolates the fluid contacting and coated side of the sensor from the interior of the housing. The housing prevents fluid communication between the non-porous adherent film of the coating material formed on the fluid contacting surface of the sensor from a second fluid isolated surface of the sensor which may have circuit elements, bonding pads, and other structures deposited onto it. The device can have a sensor with a formed adherent protective coating that has a surface energy of less than 30 dynes/cm. The housing used to mount one or more sensors may include fluid inlet and fluid outlet connections. The device may include sensor materials which include but are not limited to piezoresistive, piezoelectric, thermoresistive or a combination of these properties. Preferably the device has a sensor where the non-porous (evaporated) film of the coating material formed on the surface of the sensor includes greater than 10% of the poly-oligomer in the coating material deposited on the sensors to form the film; little or no coating material is lost during the deposition and non-porous film forming process. Even more preferably, nearly all or, 100% of

the poly-oligomer in the coating material that is deposited on the sensor to form the coating film remains on the sensor surface; no reclamation or recycling of valuable perfluorinated coating materials or coupling agents etc. is needed, nor are excessive amounts of volatile perfluorinated solvents associated with waste streams discharged. The device and mounted sensor may be used to measure one or more fluid properties such as but not limited to temperature, flow, purity, chemical composition, pressure, or a combination of these. The device in a preferred embodiment has a sensor that is coated with a poly-oligomer that includes a fluorine containing aliphatic ether ring structure in the poly-oligomer chain.

[0016] Another embodiment of the present invention is a sensing device for measuring the flow of a fluid comprising: one or more sensors, each sensor having a surface with an effective thickness of an adherent protective coating on a surface of the sensors for contacting a fluid to be measured. The coating including a soluble poly-oligomer containing fluorine, the poly-oligomer chemically bonded to the sensor surface to form an adherent protective coating. The adherent coating is formed by curing a non-porous film of the coating material deposited on the fluid contacting surface of the sensors. The device can include a conduit for directing fluid so that it contacts the coated sensor surface. Structures or means for applying energy, i.e. exciting the sensing device and means or structures for measuring said physical response from the sensors may be present on a surface of the sensors. The device includes a housing that is configured to prevent fluid communication between the non-porous adherent film of the coating material formed on the fluid contacting surface of the sensors and a second fluid isolated surface of the sensors. Each said sensor fluidly sealed to the housing and separated one from the other by a fluid conduit. Preferably the sensors in the device have a film of the coating material formed on the surface of the sensors that includes greater than 10% of the poly-oligomer in the

coating material deposited on the sensors to form the film. The sensors in the device may have an adherent protective coating in their surface which has a surface energy of less than 30 dynes/cm. The device can have sensors that include but are not limited to a material chosen from the group consisting of a piezoresistive, piezoelectric, ceramic, a metal, or a combination of these. The fluid conduit separating said sensors in the device may be a tube and the sensors are pressure sensors. The fluid conduit separating said sensors in the device may be a ventruri and the sensors are pressure sensors. The fluid conduit separating said sensors in the device can be an orifice and the sensors can be pressure sensors. The fluid conduit separating the sensors in the device can be is a tube and the sensors can be pressure sensors. The fluid conduit may be a laminar flow element from a thermal mass flow meter, where the conduit is coated on its fluid contacting inner diameter with the coating material to form the effective thickness of an adherent protective coating on the surface of the sensors for contacting a fluid to be measured; the resistive heating and temperature sensing elements of a thermal flow sensor are wound or deposited on the outside of the tube.

[0017] Another embodiment of the present invention is a sensing device that includes a sensor having a surface with an effective thickness of an adherent protective coating. The coating including a soluble poly-oligomer with a fluorine containing aliphatic ether ring structure in the poly-oligomer chain. The poly-oligomer chemically bonds to a sensor surface to form an adherent coating. The adherent coating may be formed by curing a non-porous evaporated film of the coating material formed on or deposited on the surface of the sensor to be coated and in contact with the fluid. Preferably curing occurs at a temperature less than the boiling point of the coating material solvent and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-

oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. The non-porous film of the coating material formed on the surface of the sensor in the device preferably includes greater than 10% of the poly-oligomer in the coating material deposited on the substrate to form the non-porous film. The sensing device preferably has a coating on the sensor of effective thickness to protect the underlying sensor from corrosion, erosion, delamination, or particle generation and the adherent protective coating permits the sensor to produce a measurable physical response to a fluid property.

**[0018]** Another embodiment of the present invention is a method of making a coated sensor that includes applying or depositing an amount of a coating material without entraining bubbles in the coating material on a chemically bondable fluid contacting surface of a sensor. The coating material includes a solvent, a soluble poly-oligomer having a fluorine containing groups and an aliphatic ether ring in the chain of the poly-oligomer, and the poly-oligomer has reactive groups. The reactive groups on the poly-oligomer are used for bonding the poly-oligomer to the chemically bondable fluid contacting surface of the sensor. The method has a step of removing solvent from the coating material applied to the chemically bondable fluid contacting surface of the sensor to form a non-porous film of said coating material. The formed non-porous film includes greater than 10% of the poly-oligomer in the coating material originally applied to the fluid contacting surface of the sensor. The method has a step of curing the non-porous film of the coating material on the chemically bondable fluid contacting surface of the sensor. The curing chemically bonds at least a portion the reactive groups of the poly-oligomer to the chemically bondable surface of the sensor surface to form an adherent non-porous protective coating on the chemically bondable fluid contacting surface of the sensor. The method may be used on chemically bondable fluid contacting surface of the sensor that may be

but is not limited to a ceramic, a mineral, a poly-oligomer, a metal or a combination of these.

Curing occurs at a temperature less than the boiling point of the coating material solvent and less than the Tg of poly-oligomer film and ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate.

Preferably the curing step occurs at a temperature below which damage to the electronic structures on other surfaces of the sensor can occur, even more preferably the curing temperature is less than 120°C. Chemical and photochemical treatments of the non-porous film may be used to cure it to the sensor surface. The chemically bondable fluid contacting surface of the sensor used in the method may be treated with an organosilane to form the chemically bondable fluid contacting surface of the sensor. The method may be used to coat one or more sensors, each sensor having a chemically bondable fluid contacting surface. The coating material can be applied to each sensor by a dispenser having one or more nozzles. The chemically bondable fluid contacting surface of the sensor used in the method may include a ceramic material or a ceramic material with a coating on it. The method preferably results in an effective thickness of an adherent non-porous coating on a surface of the sensor which protect it and structures formed on it from corrosion, particle generation, delamination, swelling, or changes in sensor response and sensitivity caused by the fluid and even more preferably has a thickness of greater than 50 microns and even more preferably greater than or equal to 100 microns. The method of coating may be used for a sensor which includes a diaphragm. The solvent removal step of the method may be performed in an antistatic environment. The curing step of the method may include but is not limited to chemical, photochemical, thermal curing or a combination of these. The sensor, coated by the method may include structure on one or more of its surfaces chosen from the group

consisting of resistive, capacitive, transistors, electrical contacts, optical contacts, or a combination of these.

**[0019]** Advantage of the present invention include the ability to form thick non-porous protective coatings on a variety of substrates in a single deposition step. The invention permits a variety of sensors, cuvettes, bellows, gas cells, optical window, material handling devices and housings, to be coated and used in hostile and corrosive environments. Preferably the adherent non porous coating protects the underlying structures from corrosion, particle generation, delamination, or changes in sensor response and sensitivity caused by the fluid. In some cases less expensive but more sensitive versions of sensors can be coated with the protective and adherent film and used in corrosive and hostile environment reducing costs and improving performance. The coating process is simple and results in fluid applied to a substrate that can be treated to form non-porous films of the poly-oligomer suitable for curing. The process minimizes waste and chemical consumption and reduces overall cost while maintaining or improving overall performance achieved through the use of low cost sensors. The ability to coat multiple sensors or other fluid contacting structures and to simplify the manufacturing process because devices can be coated having leads, electronics, and bond pads already formed on the structures by the use of a low temperature curing process condition is advantageous.

**[0020]** The defect free and adherent thick coatings made by the present invention provide greater chemical and mechanical resistance than thinner coatings applied to similar structures because diffusion and chemical permeability decrease as coating thickness increases. The ability to make such coatings in a single step makes the use of such coatings possible because of their ease of manufacture and cost effective because multiple sensors may be coated and material waste is minimized.

[0021] The coating can also help to preserve the physical integrity of a fluid system by maintaining a fluid tight seal when there is a mechanical failure of the coated substrate. As an example illustrated in FIG. 6, if a gauge type of ceramic pressure sensor is exposed to a pressure condition in excess of its pressure rating, there is a possibility that the brittle sensing diaphragm may fail and allow the process fluid to escape from the fluid system through the sensor's atmospheric vent, potentially causing damage to nearby equipment, or endangering the health of people in the area. If the sensor diaphragm is coated with a defect free, adherent material that is flexible and extensible, fluid system integrity is maintained in case of diaphragm failure. The coating also prevents contamination of the fluid system in the case of failure of the coated component.

## DESCRIPTION OF THE DRAWINGS

[0022] In part, other aspects, features, benefits and advantages of the embodiments of the present invention will be apparent with regard to the following description, appended claims and accompanying drawings where:

[0023] FIG. 1 illustrates a sensor or substrate with a coating material being dispensed without bubbles onto the substrate surface from a nozzle, electrical or optical feed-through connected to the substrate are also shown;

[0024] FIG. 2 (A) illustrates a bubble free volume of coating material deposited onto the surface of a substrate, (B) shows that coating conformally covering a sensor substrate of the present invention after evaporation of solvent to form a non-porous film suitable for curing;

[0025] FIG. 3 Calibration data for coated sensor with and without the adherent non-porous coating of the present invention at various time intervals;

[0026] FIG. 4 illustrates a process and apparatus for coating multiple substrates on a rotatable stage with a coating material dispensed from a nozzle onto the substrate surfaces.

[0027] FIG. 5 illustrates sensors having non-porous adherent coating configured in a housing for measuring the property of a fluid; the housing can be mounted in a fluid flow circuit and has inlet and outlet ports in the fluid flow path;

[0028] FIG. 6 illustrates a substrate having a non-porous adherent coating on the surface opposite the sensor base.

[0029] FIG. 7 illustrates a fluid handling device having one or more sensors , portions of the surfaces of the sensor and or fluid handling device may be coated with a porous inert coating.

### **DETAILED DESCRIPTION**

[0030] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular molecules, compositions, methodologies or protocols described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

[0031] It must also be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to a “coating poly-oligomer molecule” is a reference to one or more coating poly-oligomer molecules and equivalents thereof known to those skilled in the art, and so forth. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing



of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

**[0032]** Embodiments of the present invention include adherent coatings of chemically inert high purity poly-oligomers on sensor and other substrates. The coatings are applied and cured on the sensor or other substrates at relatively low temperatures which permits the coating process to be performed with temperature sensitive substrates having low melting points, magnetic properties, sensitive electronics for conversion of the substrate properties into electrical signal. Structures of the present invention include those having an effective thickness of a protective non-porous coating that is adherent and chemically bonded surface of the structure in contact with a fluid. Structures may include but not limited to a sensor, a conduit, a vessel such as a cuvette or gas sampling cell, mixers, bellows, impellers, diaphragms, fluid material handling, or wafer handling equipment, or transparent windows that are to be contacted with a fluid during chemical processing, transport, handling, or characterization. The fluid can be one whose properties are to be measured or characterized. The protective and adherent coating is chemically inert, has low permeability to fluids, ions and gases. An effective thickness adherent non-porous coating on a surface of the sensor protect it and structures formed on or within the substrates such as magnets, electrodes and electrical structures from corrosion, particle generation, delamination, swelling, or other physical and chemical changes that may adversely affect the performance or operation of the underlying coated substrate.

**[0033]** The coating may be applied to various devices that include a housing having at least one fluid chamber, the chamber in fluid communication with a fluid inlet to the housing and

the chamber in fluid communication with an fluid outlet from the housing. The chamber can include one or more structures capable of interacting with fluid in the chamber such as a flow sensor, a bellows, or an impeller. One or more surfaces of structures in the device, such as but not limited to the housing, the chambers, the inlet and outlet, bellow, impellers, pressure sensor and combinations of these can have an effective thickness of a non-porous adherent protective coating on at least a portion of a surface, the coating protecting the surface from a fluid, the coating including a soluble poly-oligomer containing fluorine, and being chemically bonded to the surface. The device may have structures interacting with the fluid in the chamber that can be a diaphragm, a bellows, an impeller, a sensor or combinations of these. The device housing, chamber, and structures can interact to form a pump, a valve, a fluid flow meter, or a fluid flow controller. The housing, chamber, and structures can interact with the fluid form a valve. The the housing, chamber, and structures can interact to form a fluid flow meter. The housing, chamber, and structures of the device can interact to form a fluid flow controller.

[0034] Bellows can used to create a seal around a moving part such as vertical driver and may be used in a variety devices like pumps, valves, and robotic arms. In pumps for example, when pressurized air is directed by a valve through a first conduit to the interior of a cylinder in contact with a piston that is surrounded by a bellows, the bellows is raised and the extension of the bellows can be used to dispense a liquid through an outlet via a check valve and to transport liquid through a connection to a first liquid chamber. The pressurized air can then be directed by the valve into a second conduit, releasing pressure on the cylinder interior and used to lower or contract the bellows to discharge liquid in the liquid chamber and to draw fluid from a source into a second liquid chamber separates from the first by the connection. This cycle of directing pressurized air into the first and second conduits can be repeated to pump a liquid. By

fabricating a valve seat in the housing and a stem on the end of the bellows, a similar cycle could be used to open and close a valve. Bellows high surface area and motion can trap contaminants, require long purge times, create stress in the bellows and corrosion of the bellows can result in particle generation.

**[0035]** Other objects, such as encased magnetic stirrers, magnetic pump impellers, and magnetically levitated impellers, when used in an ultrapure but corrosive environment, require a superior chemically resistant, non-permeable, and low diffusion coating. Coating methods for devices such as these and others which require a 360 degree coating may be drip coated, immersion coated, or coated while magnetically suspended in place. In the case of drip or immersion coating, a second coating may be necessary where supports were used in the first coating to ensure a defect free final coating.

**[0036]** To obtain wet chemical coatings with low surface roughness, it may be desirable to carry out the coating in a cleanroom, and to filter the coating liquid. Proper cleaning of the substrates is also important to remove grease, surface contaminants, and other particulates that may affect coating adhesion.

**[0037]** Dip coating techniques can be used to coat various substrates with the fluorine containing coating solution. In this process the substrate, or portion of the substrate, to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed under controlled temperature and atmospheric conditions. The coating thickness is mainly defined by the withdrawal speed, by the coating concentration (monomers, solids, gels, oligomers) and the viscosity of the liquid. The withdrawal speed of the object to be coated (conduit, sensor, bellows, housing, impeller, stirrer, mixer, portions of these, and combinations of these) may be chosen such that the sheer rates of the coating composition keep the system in the Newtonian

regime. Under these conditions it may be possible to estimate the desired coating thickness using Landau-Levich equation and routine experimentation. Variations in the coating thickness may also be achieved by changing the viscosity of the coating solution, the solution density. Because the atmosphere surrounding the item being coated controls the evaporation of the solvent and the formation of the final film, the addition, removal, or modification of solvent vapor pressure near the substrate object to be coated can also be used to control the coating thickness. An angle-dependent dip coating process can be used to coat the objects or substrates. In this process the coating thickness can be changed by modification of the angle between the substrate and the liquid surface. In this process, the substrate or object can be rotated at an angle in a vessel containing the coating material. Layer thickness and uniformity can be calculated and related to the dipping angle, withdrawal rate, and rotation rate for the substrate. These coating variables can be changed to obtain an adherent non-porous layer of the fluorine containing material coating following backing that protects the underlying object surfaces from fluids that would adversely affect the underlying substrate surface (corrosion, delamination, particle generation, swelling, weakening, generation of contamination).

[0038] Substrates may be coated in a flow coating process where the liquid coating composition is essentially poured over the substrate to be coated. The coating thickness depends on the angle of inclination of the substrate with the liquid coating composition dispense stream, the coating liquid viscosity and the solvent evaporation rate. Flow coating processes may be used to recapture coating material that does not adhere to the substrate. The atmosphere of the chamber with the object and bath may be controlled. Using the flow-coating process, non-planar large substrates can be coated rather easily. As a variation of this process, the spinning of the substrate after coating may be helpful in order to obtain more homogenous coatings.

[0039] Withdrawal speeds of substrates being coated in a dip-coat process can range from as low as 0.1 mm/min upto about 3 cm/second.

[0040] High purity poly-oligomers containing fluorine or coatings made from them of are preferably those which do not contribute amounts materials considered to be contaminants in the fluid to be contacted with the coated substrate. Preferably the coating materials or the cured coatings contribute less than 1000 ppb v/v of materials considered to be contaminants to the fluid contacted by the coated substrate. Examples of such contaminants may include ions, water or organic solvents, or particulates. Soluble coating materials or formed coatings may analyzed as neat samples or following extraction using mass spectroscopic techniques, elemental analysis, HPLC, or other techniques. Where it is difficult to obtain high purity soluble coating materials, ion exchange or extraction of deposited coating may be performed to make coatings with acceptable levels of purity.

[0041] Bonding pads may be on one or more surfaces of the substrate and used to provide for input and output of electrical and or optical signals from the substrate to processors, amplifiers, through wires or optical fiber. An example of such a sensor is a strain gauge where the resistive elements are applied to the surface of the sensor that is not in contact with the fluid to be measured. In the case of an optical pressure sensor, for example, bonding pads and or electronics are not present on the surface of the substrate. In this case the substrate surface itself or the surface with a reflective coating may be used for measurement.

[0042] The pressure sensor of the present invention may be constructed as a piezoresistive or capacitance sensor having a sensing diaphragm. The sensing diaphragm is made of a etched silicon, a ceramic, a metal, or sapphire. The sensor may have a backing plate,

sensing diaphragm, silica glass bond between the backing plate and diaphragm, and electrical leads.

**[0043]** A pressure sensor may include a backing plate, a non-porous diaphragm, a sensing element adjacent an inner surface of the diaphragm, and a glass layer of a high strength material that is bonded by glassing to the backing plate and the non-porous diaphragm. The backing plate provides rigidity to the structure. The rigidity of the backing plate resists stresses transmitted from the housing to the sensing elements on the sensor diaphragm. Although the backing plate is not in direct contact with the process medium it is required to be mechanically stable and amenable to high temperature processes. The thermal expansion rate of the backing plate should approximate closely that of the sensing diaphragm. While it is possible to compensate for thermal effects, a large mismatch will produce stresses during manufacture that may cause the bond between the two pieces to yield over time. Those skilled in the art will appreciate that the non-porous diaphragm may include a Wheatstone bridge or a conductive layer formed thereon as part of a piezoresistive or capacitive type sensor respectively.

**[0044]** To form a piezoresistive sensor a silicon layer is formed on an inner surface of the non-porous diaphragm, wherein a strain gage such as a Wheatstone bridge is formed thereon. The backing plate includes apertures extending therethrough, the apertures being adapted and may contain optical or electrical leads coupled to the sensing element. A change in pressure near the non-porous diaphragm is detectable by the sensing element. An increase and decrease of pressure against the diaphragm causes deflection of the diaphragm which in turn changes the resistances of the strain gage. The changes in resistance is correlated with the pressure adjacent the diaphragm.

**[0045]** Those skilled in the art will appreciate that the backing plate and non-porous diaphragm are constructed of materials having similar thermal expansion rates to avoid unnecessary stress through a wide range of temperatures. As described below in greater detail the pressure sensor may be constructed such that the sensing element may detect an absolute pressure or gage pressure.

**[0046]** The pressure sensor may includes bond pads formed on the diaphragm between the glass layer and the non-porous diaphragm. Without limitation, the preferred embodiment of the bond pads comprise a titanium layer and a diffusion barrier. The doped silicon thin film interconnects the bond pads in a known suitable manner to form the Wheatstone bridge. A window is formed in the glass layer and backing plate, thereby providing access to bond pads. Electrical leads extend through the windows formed in the glass layer and backing plate and the electrical leads are brazed to the bond pads. The electrical leads are brazed to the bond pads and the glass layer is glassed to the diaphragm and backing plate.

**[0047]** In an alternate embodiment the diaphragm and sensing element is modified to create a capacitance rather than a piezoresistive sensor. The thin sensing diaphragm, which flexes when pressure is applied, has a capacitive plate formed on the inner surface of the sensing diaphragm and another capacitive plate is formed on the inner surface of the backing plate. One electrical lead is connected to the capacitive plate formed on the inner surface of the sensing diaphragm and another lead is electrically coupled to the inner surface of the backing plate. As the spacing between the diaphragm and the plate vary with pressure the capacitance of the plates changes. This variation in capacitance is detected by an electrically connected sensing element of known suitable construction.

**[0048]** In yet another alternative embodiment the diaphragm and sensing element are modified to accept an optical fiber. The optical fiber measures the change in shape of the diaphragm as it changes with pressure. This variation in diaphragm shape is detected by light energy from the optical fiber reflected from the fluid isolated side of the diaphragm and related to fluid pressure.

**[0049]** Methods, means, and structures for exciting sensors and detecting a response are described. Examples of such are disclosed in U.S. Patents: 6,681,787, 'System and method of operation of a digital mass flow controller', Tinsley, et al; 6,640,822, 'System and method of operation of a digital mass flow controller' Tinsley, et al; 6,617,079, 'Process and system for determining acceptability of a fluid dispense', Pillion, et al; 6,596,148, 'Regeneration of plating baths and system therefore', Belognia, et al; 6,575,027, 'Mass flow sensor interface circuit', Larsen, et al; 6,527,862, 'Flow controller', McLoughlin, et al; 6,449,571, 'System and method for sensor response linearization', Tarig, et al; 6,445,980, 'System and method for a variable gain proportional-integral (PI) controller', Vyders; the contents of each of these patents are incorporated herein by reference in their entirety.

**[0050]** The coating material is a chemically inert poly-oligomeric material having low surface energy, below about 40 dynes/cm, low chemical permeability to dissolved ions, liquids, and gases, low mass change, incompressible. The poly-oligomer chain has pendant groups that contain fluorine and can be dissolved in a solvent. The protective films preferably are those which can be characterized as having a gas permeability less than Teflon AF® for a test gas such as oxygen or nitrogen. Alternatively non-porous adherent films of the present invention may be characterized for permeation through a sample of the membrane film in contact with a temperature controlled volume of fluid and measuring permeation as a function of temperature,



fluid properties, or film thickness, by connecting the outside of the membrane to a detection system like and FTIR spectrometer or an APIMS. Examples of soluble poly-oligomers containing fluorine which may be used as coating material include those disclosed in U.S. Pat. No. 6,201, 085 the contents of which are incorporated herein by reference in their entirety. These coating materials include those which are a perfluoro-poly-oligomer obtained by the cyclo-poly-oligomerization of perfluoro(alkenyl vinyl ether). This poly-oligomer containing fluorine is soluble in organic solvents due to its amorphous structure, and may be coated onto a substrate. The substrate may be any material with which the material can form an adherent film. For example, the substrate may be treated with an adhesion promoter such as an amino-silane coupling agent and then coated with the perfluoro-poly-oligomer. Alternatively the end groups of the perfluoro-poly-oligomer are modified to provide chemical groups that provide adhesion to the substrate as disclosed in U.S. Pat. No. 5,498,657 the contents of which are incorporate herein by reference in their entirety. For example, the endgroups of the poly-oligomer chain may be modified with an organo-silane which can be used to bond the modified perfluoro-poly-oligomer to the substrate. The use of an adhesion promoter or chemically modified poly-oligomers reactive with the substrate or sensor provides adhesion of the poly-oligomer to the substrate and by reacting with substrate surface groups may help to reduce corrosion of the substrate surface. Other useful soluble poly-oligomers containing fluorine pendent groups for coatings may include those disclosed by French et. al, Journal of Fluorine Chemistry, vol 122 (2003) whose end groups can be chemically modified to promote bonding with the substrate surface or may be combined with an adhesion promoter to form adherent films with the substrate.

**[0051]** The use of an adhesion promoter in accordance with the present invention advantageously avoids the disadvantages attendant upon forming separate barrier/passivation

layers and separate adhesion layers. In accordance with the present invention, any of various commercially available adhesion promoters can be employed, such as but not limited to silane-based organic adhesion promoters. Suitable commercially available silane-based adhesion promoters include 3-APS (3-aminopropyltriethoxysilane) or MOPS (3-methacryloxypropyltrimethoxysilane). Other commercially available silane-adhesion promoters containing vinyl, chloropropyl, epoxy, diamine, mercapto and/or cationic styryl organofunctional groups can be employed. Where chemically acceptable, non-silicon adhesion promoters containing for example aluminum, gallium, or other elements may be used.

**[0052]** The coating material dissolves in a solvent. The coating material may include fluorine containing poly-oligomers with alicyclic structures in its main chain and preferably fluorine containing aliphatic ether ring structures in its main chain. The chain of the poly-oligomer in the coating material may have reactive groups for bonding to the substrate. The coating material poly-oligomer may have molecules such as but not limited to amino functionalized organosilanes dissolved in the coating material that may bond to the substrate and to reactive groups on the poly-oligomer chains for bonding the poly-oligomer to the substrate. The coating material poly-oligomer may have reactive groups for bonding to the substrate and for bonding with other poly-oligomer chains.

**[0053]** The molecular weight of the poly-oligomer in the coating material may be used to tailor the coating for surface coverage, adhesion, strength, and chemical permeability. The concentration of the poly-oligomer used in the coating solution will affect its dispense, viscosity, and the thickness of a formed film for a given amount of coating material deposited on a substrate. The concentration of poly-oligomer in the solution depends upon the molecular weight of the poly-oligomer, but may be less than about 50% and is preferably less than about

25% by weight. The density of the the adherent non-porous coating film may be controlled by the concentration of the poly-oligomer in the coating solution as well as by its molecular weight; increasing the poly-oligimer concentration, use of mixtures of fluorine containing poly-oligomers, or increasing the molecular weight may be used to change film density

**[0054]** The coating material includes poly-oligomeric molecules and may be used to refer to both poly-oligomeric molecules and oligomeric molecules; however the present invention may be practiced with oligomeric molecules, or a mixture of oligomers and poly-oligomers.

Oligomers which may be used include those fluorine containing molecules with reactive groups similar to those present in the poly-oligomer or poly-oligomeric molecule disclosed herein and especially those reactive groups which may be used to form higher molecular weight poly-oligomeric species upon thermal, chemical, or photochemical curing of an oligomeric coating material.

**[0055]** The purity of the coating material including but not limited to hydrocarbons, metal ions, and anions is high to prevent unwanted contamination of fluids measured by the sensor of the present invention. It may also be possible to clean deposited films for example by chemical extraction or vacuum baking and degassing to achieve a higher purity in finished films.

**[0056]** Materials for coating the substrates, and preferably sensor substrates, of the present invention may include those which cure and adhere by chemical bonding to the substrate, form defect free (cracks, voids, bubbles) films of sufficient thickness to provide the substrate with chemical protection and not attenuate the sensitivity of the sensor in its application. The materials may be applied at temperatures and processing conditions which are compatible with sensors having electronic circuitry formed on a portion of the substrate. Curing the non-porous film can occur at a temperature less than the boiling point of the coating material solvent and less

than the Tg of poly-oligomer film followed by ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the poly-oligomer material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. It is desirable that the coating form a uniform film that adheres to the sensor substrate at temperatures below about 200 °C and more preferably below about 120 °C.

**[0057]** The temperature for drying the fluorine-containing solvent and fluorine containing poly-oligomer is selected depending upon the heat resistance of the substrate, and may range from 15 °C to about 150 °C; and preferably is below 35 °C. To prevent an irregular film thickness the solvent may be removed in an antistatic environment. Evaporation of solvent from the coating material composition forms a non-porous film of the poly-oligomer from the coating material on the substrate. Preferably the film of the coating material on the substrate is non-porous so that fluids or particles cannot pass through the film except by permeation or diffusion. The coating material film on the substrate, and preferably a non-porous film, may be cured to form the adherent film of the coating material on the surface of the substrate. Long curing times may be used to achieve reaction of the adhesion promoter at lower temperatures. Lower curing temperature permits substrates with deposited electronics to be coated and processed directly which provides for low cost production methods and permits less expensive electronics to be used.

**[0058]** Preferably the adherent non-porous coatings have a low permeability for ions, water, and other fluids so that fluids to be measured are prevented from contacting the substrate and the coating mass and physical properties are maintained. Also, the cured coatings preferably do not attenuate the signal of the sensor and maintain sufficient rigidity.

**[0059]** The coating material may be deposited, applied, or dispensed onto the substrate by low temperature coating processes that preferably minimizes or eliminates waste of the coating material. Examples of such coating method may include but are not limited to knife over roll coating, die cast coating, immersion coating, curtain coating, and air knife coating. Where coating of the substrate utilizes a nozzle, the nozzle can be positioned over the substrate and in a proximity to the substrate so the coating material from the nozzle contacts the surface of the substrate in a continuous stream. One method of avoiding bubble generation is minimizing the velocity of the solution as it is transferred from pipette to diaphragm by careful pipetting or nozzle dispense technique. Dispense pumps such as the Intelligen® from the Mykrolis Corporation, syringe pumps such as the Harvard Model 22, or automated micropipettors can be used to dispense fluid onto substrates. The stream of fluid without the formation of drops also provides for thick coating films and minimize the entrainment of bubbles in the films which may lead to voids and corrosion paths in the coating. Multiple dies may be used for coating multiple substrates or the substrates may be moved under the die on a rotating table or a conveyer. The coating can be deposited onto the substrate at a rate so that a meniscus of the liquid forms on the sensor .

**[0060]** The coating is preferably applied to the substrate in by a method or process which minimizes and preferably eliminates the amount of coating material which is lost or wasted during the coating process. For example, in the application of coating material onto a planar electrode, the coating material is may be dispensed from a nozzle onto a stationary or slowly rotating electrode in a single continuous stream until the substrate is covered with the coating material. Alternatively a dip coating process or a flow coating process can be used. The liquid is allowed to evaporate to leave a non-porous conformal film of the coating on the substrate. By

comparison, a spin coating process, while it may be used to distribute dispensed coating material across a substrate, is less desirable because upto about 99% of the coating fluid dispensed onto the coating surface is lost during spin up.

[0061] During the dispense and subsequent evaporation of solvent from the coating material applied to the substrate the composition of the atmosphere surrounding the substrate and coating may be controlled. This may include but is not limited to control of the temperature, flow rate of gas across the coated substrate, composition of the gas to include reactive gases as well as solvent vapor, the use of an antistatic environment or a combination of any of these.

[0062] The temperature during evaporation can be in the range of from 15 C to 50 C and provides for a crack free film of the uncured poly-oligomer to form on the sensor substrate. The evaporation parameter to form the non-porous film may be determined by thermogravimetric analysis of the coating material at different temperatures and gas flow conditions. The evaporation time will depend upon the amount of material, the vapor pressure of the solvent(s), surface area, temperature of the substrate and surrounding environment, and flow rate of gases. These may be modified as would be known to those skilled in the art, however the formed film is free of defects (crack, voids, bubbles).

[0063] Once the poly-oligomer has formed a self supporting film on the substrate in may be cured to promote adhesion of the poly-oligomer to the substrate. For example it is desirable that the coating form a uniform film that adheres to the sensor substrate at temperatures below about 200 °C and more preferably below about 120 °C. The curing temperature may be slowly ramped up to the curing temperature to avoid rapid solvent outgassing and bubble formation. Ramping the temperature up to a value greater the boiling point of the solvent and greater the T<sub>g</sub> of the fluorine containing poly-oligomer removes remaining solvent in the film and to cause the

terminal groups of the fluorine containing poly-oligomer to further react, either with the ceramic substrate, promoting adhesion, or internally, crosslinking and increasing chemical resistance. This process can be carried out in an oven capable of increasing the process temperature at a rate of about 5 °C/hour, 10 °C/hour or more provided that bubbles or cracks are not form in the film as temperatures above the solvent boiling point and poly-oligomer glass transition temperature are exceeded. After heating the non-porous film on the substrate to a temperature above the solvent boiling point and poly-oligomer glass transition temperature the substrate is allowed to soak at the final temperature for about 2 hours or sufficient time to chemically bond the film to the substrate. The time required to sufficiently bond the film to the surface of the substrate may vary depending upon the substrate, final temperature, and reactivity of the adhesion promoting groups but can determined by measuring the non –porous film adhesion with a standard tape test after various temperature and times for heating. An inert gas purge may be used during the evaporation and heat treatment processes.

[0064] When water vapor or any other condensable vapor is absorbed by a poly-oligomer film, the physical properties of the film, such as mass, thickness, surface resistance, volume resistance, and dielectric constant, all change. These changes, which can be detected by various means and may be used to characterize the desirability of various coating materials. For instance, changes in the quantity of water absorbed in humidity-sensitive films can be measured as changes in 1) the resonant frequency of a surface acoustic wave or a mechanically resonant structure coated with the film, 2) the surface or volume resistance between two electrodes connected to the film, or 3) the capacitance between sandwich-electrode or interdigitated-electrode capacitors employing the film as dielectric.

**[0065]** A very wide range of substrates may be provided with a composite coating in accordance with the instant invention. Almost any organic or inorganic solid material may be suitable as a substrate, including metal, glass, ceramic semiconductors, rubber, natural and synthetic resins, etc. Especially useful are those substrates which have reactive groups, such as but not limited to hydroxyl and carboxylic acid groups that can be used to chemically react with and bond to a portion of the poly-oligomeric molecules in the coating material or an added adhesion promoter. The process of the invention is also suited for encapsulation of electrode and electronic components. The adherent non-porous films coating a portion of the substrates in contact with a fluid bonds to the surface and reduces or is non- permeable to fluids and ions in fluids which degrade or corrode the underlying substrate. The degradation may affect the physical or chemical properties of the underlying substrate for its intended purpose. The degradation may be used to prevent the release of degradation products, such as but not limited to particles, molecules, and ions, from the underlying substrate into the process fluid

**[0066]** Sensors which may be coated by the materials and methods of the present invention are preferably those on which a layer of poly-oligomer may be applied to form a thick film of the poly-oligomer on the sensor such as but not limited to die cast, aerosol spray coat, dip coating, or a combination of these. The substrates may be coated in a single step, however more than one coating step may be used to achieve a desired film thickness or to coat substrates where it is not practical to coat the entire object in a single step. Where the substrates are planar, they may include channels or raised structures on their surface. The sensor substrates may have a surface in which have reactive groups or may be chemically treated such as by plasma, pre-coating, or chemical methods to form groups on the sensor surface that can further react with reactive groups on poly-oligomer molecules in the coating material solution to bond a portion or



all of the poly-oligomer to the substrate. The poly-oligomer molecules in addition to bonding with the substrate surface, may also react with each other to form a cross linked structure. The reaction of the reactive groups of the poly-oligomer with each other or with the surface may be initiated by thermal, photochemical, or chemical treatments. For example, the thermal treatment of the substrate and poly-oligomer film can result in hydrolysis reactions between the substrate and reactive groups on the poly-oligomer.

**[0067]** Where the substrate includes one or more material interfaces between different materials a poly-oligomer coating material may be applied to the substrate and one or more interfaces to provide chemical and mechanical advantages to the substrate and interfaces. Preferably each of the surfaces are capable of or have been treated to react with an adhesion promoter or the poly-oligomer molecules in the poly-oligomer coating material to effect adhesion of the coating material to the substrate. Thermal, photochemical, or chemical reaction or a combination of these may be used to react the surfaces with coating to effect adhesion.

**[0068]** For optically transparent poly-oligomer films, a chemically sensitive material may be incorporated into a portion of the poly-oligomer molecules or the chemically sensitive material may be incorporated into the surface of the poly-oligomer film. A change in color or absorption for example may be detected by light absorbed or reflected from the coating to indicate the presence or absence of desirable or deleterious molecules in the fluid. Optical windows may be coated by the fluorine containing poly-oligomer coating material composition to provide chemical and physical protection to the window.

**[0069]** The substrates coated by the poly-oligomer may include but are not limited to pressure sensors including strain gauges, capacitive based pressure sensors, and fiber optic or laser diode based pressure sensors that measure changes in a property, such as intensity, of light

or electromagnetic energy reflected from the diaphragm surface. The substrate may serve as a support for the poly-oligomer film and any chemically sensitive material incorporated thereon. In this case the substrate and film are optically transparent in the wavelength region used for detection. The sensor may be used to measure the temperature of a fluid and the poly-oligomeric coating used to prevent or substantially reduce ions and fluid from reaching the temperature probe.

**[0070]** The sensors of the present invention may be mounted in a housing to contact the sensors with a fluid whose property is to be measured. The housing may be made of a chemically suitable material, preferably a material which is chemically inert to the fluid. Some housing materials may include a coating of the poly-oligomeric material applied to a portion or all of the housing surfaces. The poly-oligomer coated sensor or optical window in a housing or vessel may be mounted to or in the housing or vessel using methods and materials known to those skilled in the art including but not limited to compression seals using o-rings, gaskets, and fusion bonding. The housing may be placed in contact with the fluid by submersion or the housing may have inlet and outlet fluid ports for mounting the sensor in fluid communication with fluid in a conduit. The windows may be those in a gas cell used for the analysis of chemical composition of fluids, the adherent non-porous coating protecting the windows and gas cell from corrosion and particle generation.

**[0071]** The coated sensors may be combined to form flowmeters and other measuring devices such as but not limited to temperature compensated pressure sensors, flow meters, and flow rate compensated chemical sensors.

**[0072]** Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

### EXAMPLE 1

[0073] CYTOP coating of the Metallux ceramic pressure sensors to form an integral coating include applying the poly-oligomer solution onto the sensor without entraining air bubbles and slowly ramping up to the curing temperature to avoid rapid solvent outgassing and bubble formation.

[0074] Calibration data from a single Metallux pressure sensor; uncoated, with a 2.5 mil CYTOP coating and with a 5 mil CYTOP coating; there was no significant difference between any of the data sets as illustrated in FIG. 3.

[0075] Metallux data show an offset shift  $< 0.2\%$  F.S. after 2,000,000 F.S. pressure cycles and an offset shift of  $< 0.05\%$  F.S. after 110 hours at  $82^{\circ}\text{C}$ .

### EXAMPLE 2

[0076] Evaluation of chemical compatibility of Metallux pressure sensors coated with Cytop resin. Extractables data was acquired from tests using HCl, TMAH, and DI water.

[0077] The extractables levels from the tests run with DI water were all very low. The results from both the TMAH and HCl showed higher levels of aluminum and the TMAH showed high levels of lead. In both chemicals, the aluminum and lead levels were higher in the sensors coated with a **2.5mil** thick layer of Cytop, compared to the sensors coated with a **5mil** thick layer of Cytop. The aluminum levels from both chemicals were highest in the aluminum buttons coated with a 5mil thick layer of Cytop.

[0078] These tests were run using ten Teflon housings, each of which was designed to hold two Metallux pressure sensors. With the sensors installed, each unit can hold

approximately 1.5ml of fluid. When installed, the face of each of the two sensors is in contact with the fluid.

[0079] Four different materials were tested: Teflon dummy sensors with the same dimensions as the pressure sensors were used for a baseline, aluminum buttons with the same dimensions as the pressure sensors coated with a **5mil** layer of Cytop, Metallux pressure sensors coated with a **5mil** layer of Cytop, and Metallux pressure sensors with a **2.5mil** layer of Cytop. Three different chemicals were used: deionized water, 10% hydrochloric acid, and 2.5% tetramethyl ammonium hydroxide (TMAH). A description of the material and chemical tested in each unit is shown in Table 1.

[0080] Prior to the start of the experiment, the Teflon enclosures, the Kalrez o-rings used to seal the sensors in the units, and the Teflon dummy sensors were pre-extracted over night in 10% HCl. Once the materials and chemicals were installed in each unit, the ten units were placed in a 50 °C oven for one month. Periodically during the month, the units containing the aluminum buttons were tested for resistance. A multimeter was used to test the resistance across the two aluminum buttons in each of these units. The results of each measurement are shown in Table 2. No increase in resistance was observed during any of the measurements indicating that measurable amounts of ions were not generated by diffusion or permeation of ions through the films. At the end of the month, all of the chemical samples were submitted to the Analytical department for extractables testing.

[0081] The extractables results are reported in units of ug/unit, where a unit is one housing containing two sensors. The extractables levels from tests run with DI water were all below 1 ug/unit. The highest extractables were seen from the Cytop-coated aluminum button, in

which the sodium level was 0.63 ug/unit, the potassium level was 0.59 ug/unit, and the calcium level was 0.24 ug/unit.

[0082] The extractables levels from tests run with HCl were all below 1 ug/unit, except for aluminum. The aluminum levels were highest from the Cytop-coated aluminum button (5.41 ug/unit). The aluminum levels from the **2.5mil** Cytop-coated sensor (3.51 ug/unit) were much higher than those from the **5mil** Cytop-coated sensor (0.15 ug/unit). The aluminum levels from the **5mil** Cytop-coated sensor were lower than those from the Teflon button (0.42 ug/unit).

[0083] The extractables levels from tests run with TMAH were all below 1 ug/unit, except for aluminum and lead. The aluminum levels were highest from the Cytop-coated aluminum button (6.59 ug/unit). The aluminum levels from the 2.5mil Cytop-coated sensor (2.18 ug/unit) were five times higher than those from the 5mil Cytop-coated sensor (0.42 ug/unit). The aluminum levels from the 5mil Cytop-coated sensor were close to those from the Teflon button (0.31 ug/unit). The lead levels for very small in the Teflon button and Cytop-coated aluminum button (0.01 ug/unit). The lead levels from the 2.5mil Cytop-coated sensor (2.19 ug/unit) were three times higher than those from the 5mil Cytop-coated sensor (0.69 ug/unit).

Table 1  
Test Unit Description dimensions are in  
mils

Test Unit	Material	Coating Thickness (mil)	Coating Defects	Chemical
1	Aluminum #1	5	Small dot on outer edge	DI Water
	Aluminum #2	5	None	
2	Sensor #C02482/1-8	5	Small dot on outer edge	DI Water
	Sensor #C02482/1-12	5	Small dot on outer edge	

3	Teflon	N/A	N/A	HCl
	Teflon	N/A	N/A	
4	Aluminum #6	5	None	HCl
	Aluminum #4	5	None	
5	Sensor #C02482/1-13	5	Small dot on outer edge	HCl
	Sensor #C02482/1-9	5	Small fibrous imperfection near edge	
6	Sensor #C02482/1-16	2.5	None	HCl
	Sensor #C02482/1-15	2.5	None	
7	Teflon	N/A	N/A	TMAH
	Teflon	N/A	N/A	
8	Aluminum #3	5	None	TMAH
	Aluminum #5	5	None	
9	Sensor #C02300/1-10	5	Small dot on outer edge	TMAH
	Sensor #C02300/1-11	5	None	
10	Sensor #C02482/1-14	2.5	None	TMAH
	Sensor #C02482/1-17	2.5	None	

Table 2  
Aluminum Button Monitoring (Resistance Measurements):

Date	HCl	TMAH	DI Water
2/3/03	None	N/A	N/A
2/4/03	None	N/A	N/A
2/5/03	None	N/A	N/A
2/6/03	None	N/A	N/A
2/7/03	None	None	None
2/10/03	None	None	None

2/11/03	None	None	None
2/13/03	None	None	None
2/14/03	None	None	None
2/17/03	None	None	None
2/20/03	None	None	None
2/24/03	None	None	None
2/28/03	None	None	None
3/5/03	None	None	None
3/10/03	None	None	None

[0084] Sensors were extracted for 30 days in 10% HCl. Extraction volume was 1.5mL.

Samples were analyzed for metals using ICPMS.

SampleID	5SENSO07.D	5SENSO08.D	5SENSO09.D	5SENSO10.D
SampleName	sample #3	sample #4	sample #5	sample #6
SampleType	unit	unit	unit	unit
Comments	Teflon Button	Aluminum Button (5mil coating)	Sensor (5mil coating)	Sensor (2.5mil coating)
<b>Na (ug/unit)</b>	<b>1.06</b>	<b>0.04</b>	<b>0.06</b>	<b>0.10</b>
Na RSD (%)	3.17	1.30	3.46	1.58
Na IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Mg (ug/unit)</b>	<b>0.13</b>	<b>0.06</b>	<b>0.01</b>	<b>0.03</b>
Mg RSD (%)	2.69	2.69	2.75	1.93
Mg IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Al (ug/unit)</b>	<b>0.42</b>	<b>5.41</b>	<b>0.15</b>	<b>3.51</b>
Al RSD (%)	2.85	3.38	3.12	4.03
Al IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>K (ug/unit)</b>	<b>0.94</b>	<b>0.03</b>	<b>0.04</b>	<b>0.07</b>
K RSD (%)	4.84	2.57	3.41	2.36
K IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Ca (ug/unit)</b>	<b>0.39</b>	<b>0.06</b>	<b>0.07</b>	<b>0.08</b>
Ca RSD (%)	2.55	2.36	3.18	2.05
Ca IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Ti (ug/unit)</b>	<b>0.08</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>
Ti RSD (%)	3.78	1.52	2.70	3.34
Ti IDL	0.00	0.00	0.00	0.00

(ug/unit)				
<b>Cr (ug/unit)</b>	<b>0.04</b>	<b>0.01</b>	<b>0.00</b>	<b>0.01</b>
Cr RSD (%)	3.38	4.23	5.24	3.82
Cr IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Mn (ug/unit)</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>	<b>0.00</b>
Mn RSD (%)	2.81	2.79	5.27	2.87
Mn IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Fe (ug/unit)</b>	<b>0.45</b>	<b>0.05</b>	<b>0.04</b>	<b>0.04</b>
Fe RSD (%)	3.86	2.39	3.34	2.53
Fe IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Ni (ug/unit)</b>	<b>0.02</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Ni RSD (%)	2.20	6.71	2.46	3.65
Ni IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Cu (ug/unit)</b>	<b>0.12</b>	<b>0.02</b>	<b>0.02</b>	<b>0.01</b>
Cu RSD (%)	2.90	4.19	3.46	3.20
Cu IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Zn (ug/unit)</b>	<b>0.14</b>	<b>0.00</b>	<b>0.00</b>	<b>0.01</b>
Zn RSD (%)	2.18	2.79	2.31	1.29
Zn IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Pb (ug/unit)</b>	<b>0.01</b>	<b>0.00</b>	<b>0.04</b>	<b>0.35</b>
Pb RSD (%)	1.60	0.75	1.57	1.64
Pb IDL (ug/unit)	0.00	0.00	0.00	0.00

[0085] Sensors were extracted for 30 days in TMAH. Extraction volume was 1.5mL.

TMAH extractions were prepared for analysis by hotplate evaporation and reconstitution in HNO<sub>3</sub>. Samples were analyzed for metals using ICPMS.

SampleID	5SENSO03.D	5SENSO04.D	5SENSO05.D	5SENSO06.D
SampleName	sample #7	sample #8	sample #9	sample #10
SampleType	unit	unit	unit	unit
Comments	Teflon	Aluminum	Sensor (5mil	Sensor



	Button	Button (5mil coating)	coating)	(2.5mil coating)
<b>Na (ug/unit)</b>	<b>0.08</b>	<b>0.04</b>	<b>0.07</b>	<b>0.08</b>
Na RSD (%)	1.84	6.40	0.65	1.62
Na IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Mg (ug/unit)</b>	<b>0.02</b>	<b>0.02</b>	<b>0.00</b>	<b>0.00</b>
Mg RSD (%)	1.83	5.02	2.47	1.44
Mg IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Al (ug/unit)</b>	<b>0.31</b>	<b>6.59</b>	<b>0.42</b>	<b>2.18</b>
Al RSD (%)	3.65	6.21	4.43	2.69
Al IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>K (ug/unit)</b>	<b>0.05</b>	<b>0.02</b>	<b>0.03</b>	<b>0.02</b>
K RSD (%)	2.01	5.33	0.28	1.07
K IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Ca (ug/unit)</b>	<b>0.06</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>
Ca RSD (%)	2.14	5.01	1.00	1.16
Ca IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Ti (ug/unit)</b>	<b>0.01</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Ti RSD (%)	8.58	8.19	3.62	4.37
Ti IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Cr (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Cr RSD (%)	2.78	5.55	2.54	2.33
Cr IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Mn (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Mn RSD	4.15	6.18	4.81	4.06

(%)				
Mn IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Fe (ug/unit)</b>	<b>0.04</b>	<b>0.01</b>	<b>0.01</b>	<b>0.02</b>
Fe RSD (%)	3.07	5.31	2.23	3.03
Fe IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Ni (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>	<b>0.00</b>
Ni RSD (%)	2.54	2.68	1.18	2.68
Ni IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Cu (ug/unit)</b>	<b>0.01</b>	<b>0.03</b>	<b>0.01</b>	<b>0.00</b>
Cu RSD (%)	2.38	4.54	1.06	2.10
Cu IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Zn (ug/unit)</b>	<b>0.01</b>	<b>0.13</b>	<b>0.02</b>	<b>0.01</b>
Zn RSD (%)	6.79	1.34	2.32	4.60
Zn IDL (ug/unit)	0.00	0.00	0.00	0.00
<b>Pb (ug/unit)</b>	<b>0.01</b>	<b>0.01</b>	<b>0.69</b>	<b>2.19</b>
Pb RSD (%)	18.86	4.06	5.20	4.28
Pb IDL (ug/unit)	0.00	0.00	0.00	0.00

[0086]

[0087] Sensors were extracted for 30 days in water. Extraction volume was 1.5mL.

Samples were analyzed for metals using ICPMS.

SampleID	5SENSO01.D	5SENSO02.D
SampleName	sample #1	sample #2
SampleType	unit	unit
Comments	Aluminum Button (5mil coating)	Sensor (5mil coating)

<b>Na (ug/unit)</b>	<b>0.63</b>	<b>0.12</b>
Na RSD (%)	2.24	6.61
Na IDL (ug/unit)	0.00	0.00
<b>Mg (ug/unit)</b>	<b>0.04</b>	<b>0.02</b>
Mg RSD (%)	3.16	9.34
Mg IDL (ug/unit)	0.00	0.00
<b>Al (ug/unit)</b>	<b>0.08</b>	<b>0.18</b>
Al RSD (%)	2.91	6.21
Al IDL (ug/unit)	0.00	0.00
<b>K (ug/unit)</b>	<b>0.59</b>	<b>0.13</b>
K RSD (%)	2.73	6.76
K IDL (ug/unit)	0.00	0.00
<b>Ca (ug/unit)</b>	<b>0.24</b>	<b>0.09</b>
Ca RSD (%)	3.51	12.34
Ca IDL (ug/unit)	0.00	0.00
<b>Ti (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>
Ti RSD (%)	3.87	2.92
Ti IDL (ug/unit)	0.00	0.00
<b>Cr (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>
Cr RSD (%)	2.37	7.72
Cr IDL (ug/unit)	0.00	0.00
<b>Mn (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>
Mn RSD (%)	3.86	14.44
Mn IDL (ug/unit)	0.00	0.00

<b>Fe (ug/unit)</b>	<b>0.01</b>	<b>0.01</b>
Fe RSD (%)	3.07	10.80
Fe IDL (ug/unit)	0.00	0.00
<b>Ni (ug/unit)</b>	<b>0.00</b>	<b>0.00</b>
Ni RSD (%)	3.47	10.98
Ni IDL (ug/unit)	0.00	0.00
<b>Cu (ug/unit)</b>	<b>0.00</b>	<b>0.01</b>
Cu RSD (%)	7.31	34.29
Cu IDL (ug/unit)	0.00	0.00
<b>Zn (ug/unit)</b>	<b>0.01</b>	<b>0.01</b>
Zn RSD (%)	3.64	1.74
Zn IDL (ug/unit)	0.00	0.00
<b>Pb (ug/unit)</b>	<b>0.00</b>	<b>0.04</b>
Pb RSD (%)	3.48	3.82
Pb IDL (ug/unit)	0.00	0.00

### EXAMPLE 3

**[0088]** Using volumes of Cytop coating material greater than about 200  $\mu$ l, the coating material solution will spread across a sensor surface that is an octagon shape with an edge to edge length across the sensor of about 0.654 inches and area 0.35 square inches.

**[0089]** To avoid generation of small bubbles in the Cytop coating applied to the sensor surface, these bubbles expand upon heating and create void or porous films, it is preferably not to blow out the pipette tip – this always produces bubbles. Hold tip just above sensor/coating

surface to let solution drops spread w/o producing bubbles and better still without producing individual drop. Let solvent evaporate for at least 30 min. before heating in oven. A longer evaporation. time might be necessary for the second and subsequent coats

#### **EXAMPLE 4**

**[0090]** This example describes COATING METALLUX 501 CERAMIC SENSORS WITH CYTOP PERFLUOROPOLY-OLIGOMER, available from Asahi Glass Company. CYTOP<sup>TM</sup> is a perfluoro-polymer obtained by the cyclopolymerization of perfluoro(alkenyl vinyl ether and contains fluorine bonded to the carbon chain.

**[0091]** The purpose of coating the wetted surfaces of a ceramic pressure sensor with CYTOP perfluoropoly-oligomer is to enhance the chemical resistance of these surfaces thereby minimizing the risk of contaminating the process fluid coming into contact with the sensor.

**[0092]** The coating process in this example includes the steps of: cleaning and dehydrating the surface(s) to be coated, applying a bubble-free coating of CYTOP P(er)F(luoro)P(olymer) solution to the sensor surface, allowing the bulk of the solvent to evaporate at room temperature, soft baking the sensor at a temperature less than the boiling point of the coating material solvent and less than the Tg of CYTOP PFP to remove most of the remaining solvent, ramping the temperature up to a value greater than the boiling point of the solvent and greater than the Tg of the CYTOP material to remove any remaining solvent and to enhance the adhesion of the coating to the ceramic substrate. For coatings thicker than can be applied to the surface in one coat, the steps of applying, evaporating, and curing can be repeated as needed to achieve the desired thickness prior to the final bake or curing cycle.

**[0093]** Cleaning and dehydrating the surface to be coated can be performed to ensure good adhesion between the sensor and the CYTOP coating, the surfaces to be coated (sensor

diaphragm) should be scrubbed with an acetone wet wipe to remove any organic material and then flushed with a squirt (~1 ml.) of acetone to remove any remaining particulate material. The sensor should then be baked in a 110°C oven for 60 minutes to drive off any moisture. At the end of the bake cycle, the hot sensor can be placed in a dessicator to cool, and remain in the dessicator until coated.

[0094] Applying a bubble-free coating of CYTOP PFP (PerFluoroPoly-oligomer) solution to the diaphragm. The coating material is 'CTL-107M', a 7% (by weight) solution of Asahi's 'M' CYTOP perfluoropoly-oligomer (low molecular weight grade) in CT-SOLV100, a perfluoroalkane (primarily perfluoro-octane).

[0095] The coating process requires that the sensor be mounted, diaphragm up, in a fixture having an 18 mm. Diameter recess to locate the device. A 15.25 mm. diameter thru hole in the center of the recess provides clearance for the electrical connectors/cables. The recess is level to provide a uniform coating thickness. If the sensor has an electrical cable, the center of mass of the cable falls within the vertical extension of the sensor's O.D. to prevent tilting of the sensor in the fixture.

[0096] Once the sensor is properly fixtured, a volume of CYTOP solution sufficient to cover the entire diaphragm surface, but not enough to overcome the surface tension forces at the edges of the diaphragm and allow the solution to spill over the edges, is applied to the diaphragm using a precision microliter pipetter. It was experimentally determined that at least 200 µl. of solution was needed to completely cover the diaphragm surface. (The use of more dilute CYTOP 107M solutions resulted in coating thickness variations on the active surface [minimal thermal mass] area of the diaphragm, apparently due to evaporative cooling effects).

**[0097]** Exclude or immediately remove any bubbles from the solution on the diaphragm as they will form defects (pinholes or thin spots) in the coating. One method of avoiding bubble generation is minimizing the velocity of the solution as it is transferred from pipette to diaphragm by careful pipetting technique. Also, the 1 ml. pipetter tips used in the coating process have a very small opening at the tip which can result in high solution dispense velocities and the entrainment of air bubbles in the coating. By cutting back the tapered pipetter tip by about 5 mm., the diameter of the tip opening is increased enough to minimize the generation of bubbles due to high dispense velocities. Visible bubbles in the liquid coating may be moved to the edge of the diaphragm with the pipetter tip or sucked into the pipetter; however these actions may result in the formation of small, visually undetectable bubbles which eventually become defects in the coating.

**[0098]** Allowing the bulk of the solvent to evaporate at R.T. After the bubble-free coating of CYTOP PFP solution has been applied to the sensor diaphragm, the bulk of the CT SOLV-100 is allowed to evaporate at R.T. for approximately 30 minutes before moving the sensor. This will result in a sensor with a physically stable coating precursor which can be safely transferred to the 'softbake' or curing oven.

**[0099]** 'Soft' baking the sensor at a temperature less than the boiling point of the solvent and less than the Tg of CYTOP to remove most of the solvent. The boiling point of the CT-SOLV100 solvent is about 100 °C and the Tg of the CYTOP poly-oligomer is 108 °C. The purpose of this process step is to remove most of the solvent in the coating without initiating further reaction of the poly-oligomer's end groups in preparation for additional coatings or the final bake step. This step is preferentially carried out with the sensor in the same (or a similar)

fixture as used in the coating process to keep the sensor essentially level while ramping up from a temperature of 40 °C to a temperature of 60 °C over a period of 60 minutes.

**[00100]** The three previous coating, evaporation and soft bake' steps may be repeated as needed to achieve the desired final coating thickness

**[00101]** Ramping the temperature up to a value greater the boiling point of the solvent and greater the Tg of CYTOP removes remaining solvent in the film and enhance the adhesion of the coating film to the substrate. The purpose of this step is to remove any remaining solvent from the diaphragm's coating and to cause the terminal groups of the CYTOP 'M' poly-oligomer to further react, either with the ceramic substrate, promoting adhesion, or internally, crosslinking and increasing chemical resistance. This process is carried out in an oven capable of increasing the process temperature at a rate of about 5 °C/hour from 60 °C to 125 °C, followed by a 2 hour 'soak' at 125 °C.

#### **EXAMPLE 5**

**[00102]** This prophetic example illustrates an example of a material handling device used for transporting fluid that has one or more structure coated with an adherent non-porous coating. The device includes a housing that can be used to mount one or more optional sensors and include fluid inlet and fluid outlet connections.

**[00103]** The material handling device may may be coated and used in hostile and corrosive environments. The adherent non porous coating applied to the device protects the underlying structures from corrosion, particle generation, delamination, or changes operation caused by the fluid. The ability to coat multiple fluid contacting structures and to simplify the manufacturing process because devices can be coated having leads, electronics, bond pads, or temperature sensitive magnetic elements already in or already formed on the structures is possible by the use of a low temperature curing process condition. Lower cost materials may be



used to make the impeller that can then be coated with the fluorine containing coating. Fully encapsulated impellers can be prepared at low temperatures.

**[00104]** The material handling device illustrated in FIG. 7 is an impeller pump. Structures of the impeller pump that can be coated may include but not limited to one or more optional sensors mounted to the housing, the interior of an inlet and an outlet conduit, the inner surfaces of the housing vessel, and fluid handling impellers. The impellers may be fixed or flexible.

**[00105]** The impeller structure, or portions of it, for example vanes, or vanes and supporting structure with magnets, may be coated. An adhesion promoter can be used to pre-treat the impeller surface. The impeller can be coated by angle dependent dip coating with slow rotation the portion of the impeller below the rotation shaft of the impeller (shaft not shown in FIG. 7) in a solution of CYTOP PFP (PerFluoroPoly-oligomer). This coating material is CTL-107M, a 7% (by weight) solution of Asahi's 'M' CYTOP perfluoropoly-oligomer (low molecular weight grade) in CT-SOLV100, a perfluoroalkane (primarily perfluoro-octane). The rotation rate is chosen to prevent entrapment of gas during submersion of the object and to facilitate coalescence and rising of bubbles on the impeller in the coating solution. Stands having through holes for the rotation shaft may be used to cure the first coating. The rotation shaft may be dip coated in the same solution in a second step.

**[00106]** The impeller pump may be used to handle fluids such as slurries and corrosive liquids. The coating methods of this example may be applied to other material handling devices such as diaphragm pump surfaces, bellows pump surfaces, mixing blades, and other surfaces of fluid handling devices where a low cost protective coating is needed to protect the underlying substrate.

**[00107]** Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contain within this specification.

## CLAIMS

What is claimed is:

1. An article comprising:

a substrate including an effective thickness of a non-porous adherent protective coating on at least a portion of a surface of the substrate, the coating protecting the substrate from a fluid, the coating including a soluble poly-oligomer containing fluorine, and being chemically bonded to said surface.

2. The article of claim 1 where the surface is first pretreated with an adhesion promoter.

3. The article of claim 1 where the surface is coated by dip coating.

4. The article of claim 1 where the coating material is perfluoroalkane.

5. The article of claim 1 further including magnets, a sensor, or a flow element.

6. The article of claim 1 wherein the article has a rotatable shaft.

7. The article of claim 1 wherein the article is an impeller.

8. The article of claim 1 wherein the more than one surface of the article is coated.

9. A device comprising:

a housing having at least one fluid chamber, the chamber in fluid communication with a fluid inlet and in fluid communication with a fluid outlet;

one or more structures capable of interacting with fluid in the chamber; and

one or more surfaces of the device having an effective thickness of a non-porous adherent protective coating on at least a portion of a surface, the coating protecting the surface from a fluid, the coating including a soluble poly-oligomer containing fluorine, and being chemically bonded to said surface.

10. The device of claim 9 where the structures interacting with the fluid in the chamber is a diaphragm, a bellows, an impeller, a sensor or combinations of these.

11. The device of claim 9 where the housing, chamber, and structures interact to form a pump, a valve, a fluid flow meter, or a fluid flow controller.
12. The device of claim 9 where the housing, chamber, and structures interact to form a valve.
13. The device of claim 9 where the housing, chamber, and structures interact to form a fluid flow meter.
14. The device of claim 9 where the housing, chamber, and structures interact to form a fluid flow controller.
15. The device of claim 9 where the soluble poly-oligomer containing fluorine is a perfluoroalkane.
16. An article consisting essentially of:
  - a substrate having an effective thickness of a non-porous adherent protective coating on at least a portion of a surface of the substrate, the coating protecting the substrate from a fluid, the coating including a soluble poly-oligomer containing fluorine, and being chemically bonded to said surface.
17. The article of claim 16 where the substrate surface is first pretreated with an adhesion promoter.
18. The article of claim 16 where the surface is coated by dip coating.
19. The article of claim 16 where the coating material is perfluoroalkane.
20. The article of claim 16 where the substrate has one or more magnets, is a sensor, or is a flow element.
21. The article of claim 16 wherein the article has a rotatable shaft.
22. The article of claim 16 wherein the article is an impeller.
23. The article of claim 16 wherein the more than one surface of the article is coated.
24. The article of claim 16 wherein the article is a sensor.
25. The article of claim 16 wherein the article is a surface of a pump, a mixer, a flow meter, or a flow controller.
26. The article of claim 16 wherein the article has magnets, bond pads, or other thermally sensitive structures on the surface or within the substrate.

### **ABSTRACT OF THE DISCLOSURE**

The present invention include non-porous adherent coatings of chemically inert high purity poly-oligomers deposited on substrates. The coatings are applied and cured on the substrates at relatively low temperatures which permits the coating process to be performed with temperature sensitive structures such as magnets, electronic circuits, electrodes, and bonding pads in place on the substrate. Coated substrates, such as sensors and fluid conduits, have an effective thickness of the protective non-porous coating that is chemically bonded to a surface of the substrate that will be contacted with a fluid. The adherent non-porous coating on the substrate protect it from corrosion, particle generation, swelling, or delamination of structures on the substrate caused by contact with the fluid.

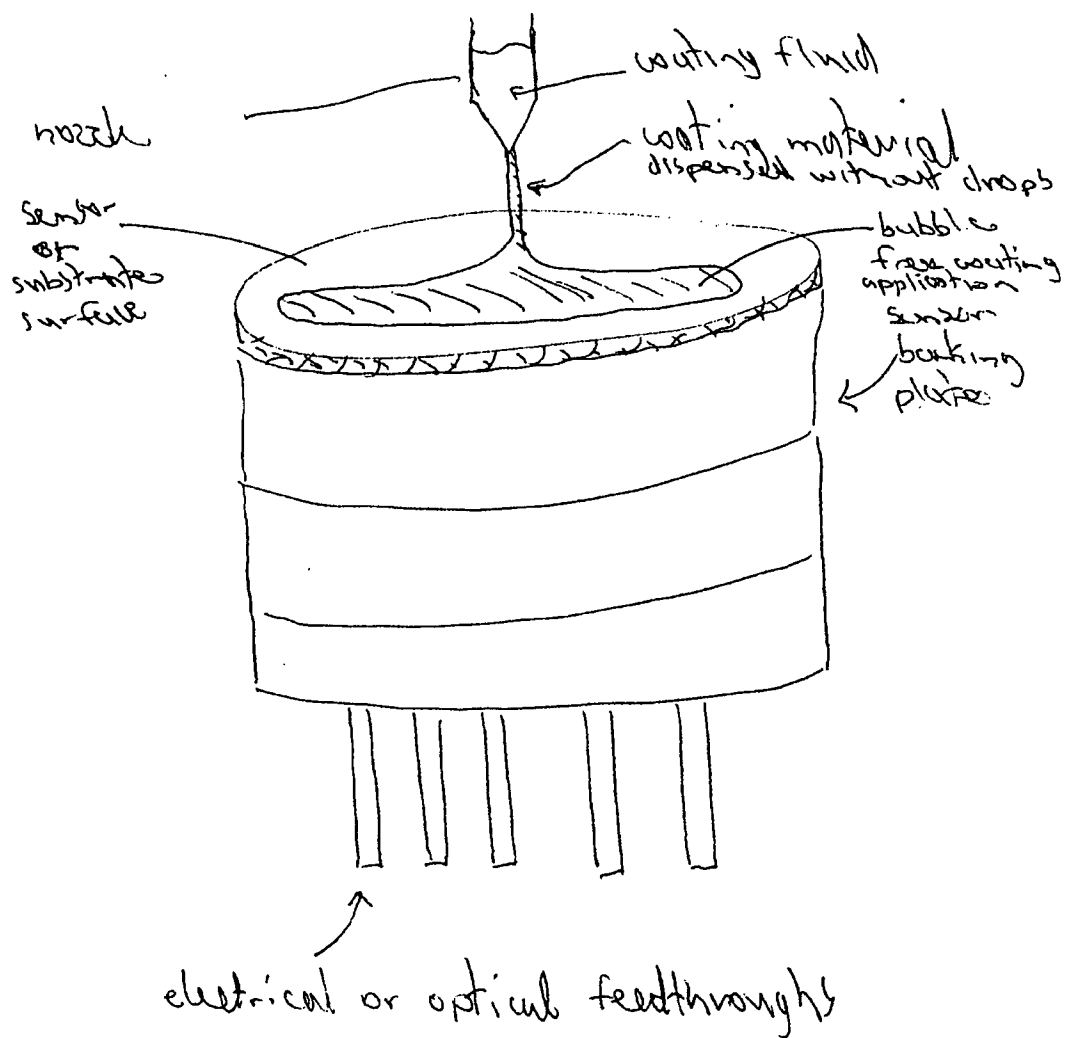
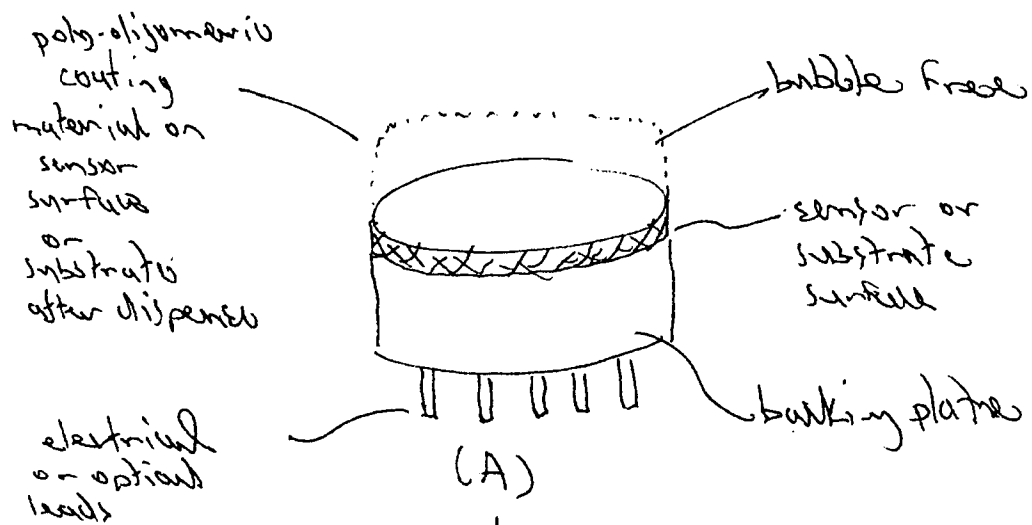


FIG. 1



evaporation/solvent removal @ RT or below 55°C

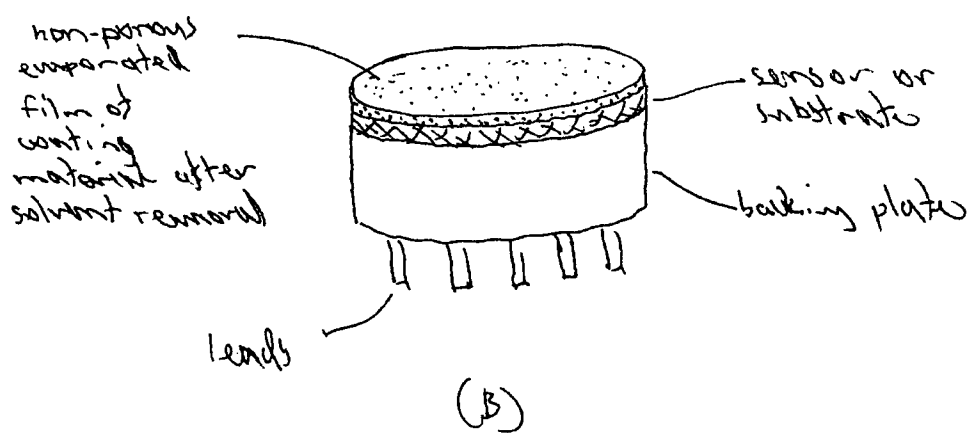
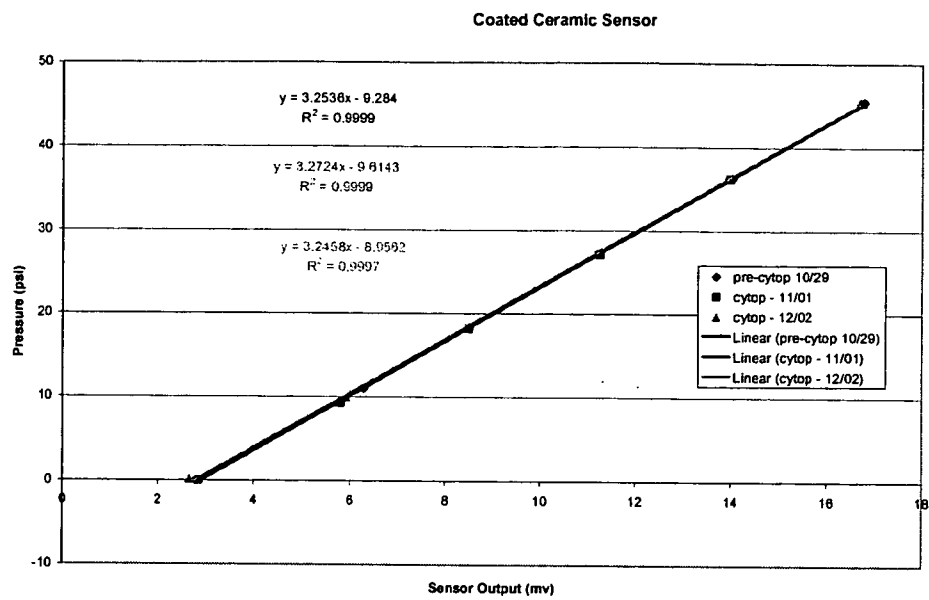


FIG. 2



**FIG. 3**  
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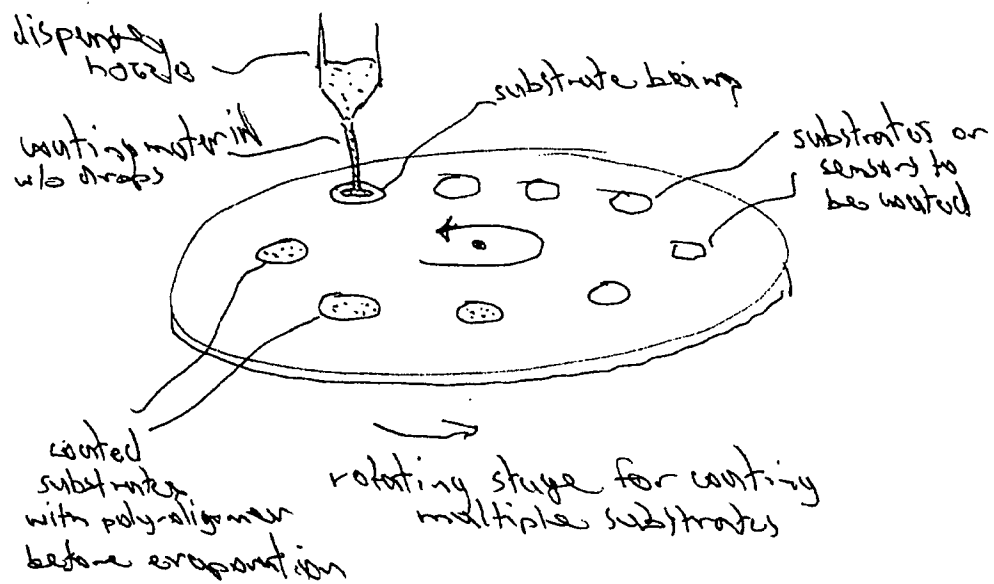


FIG. 4

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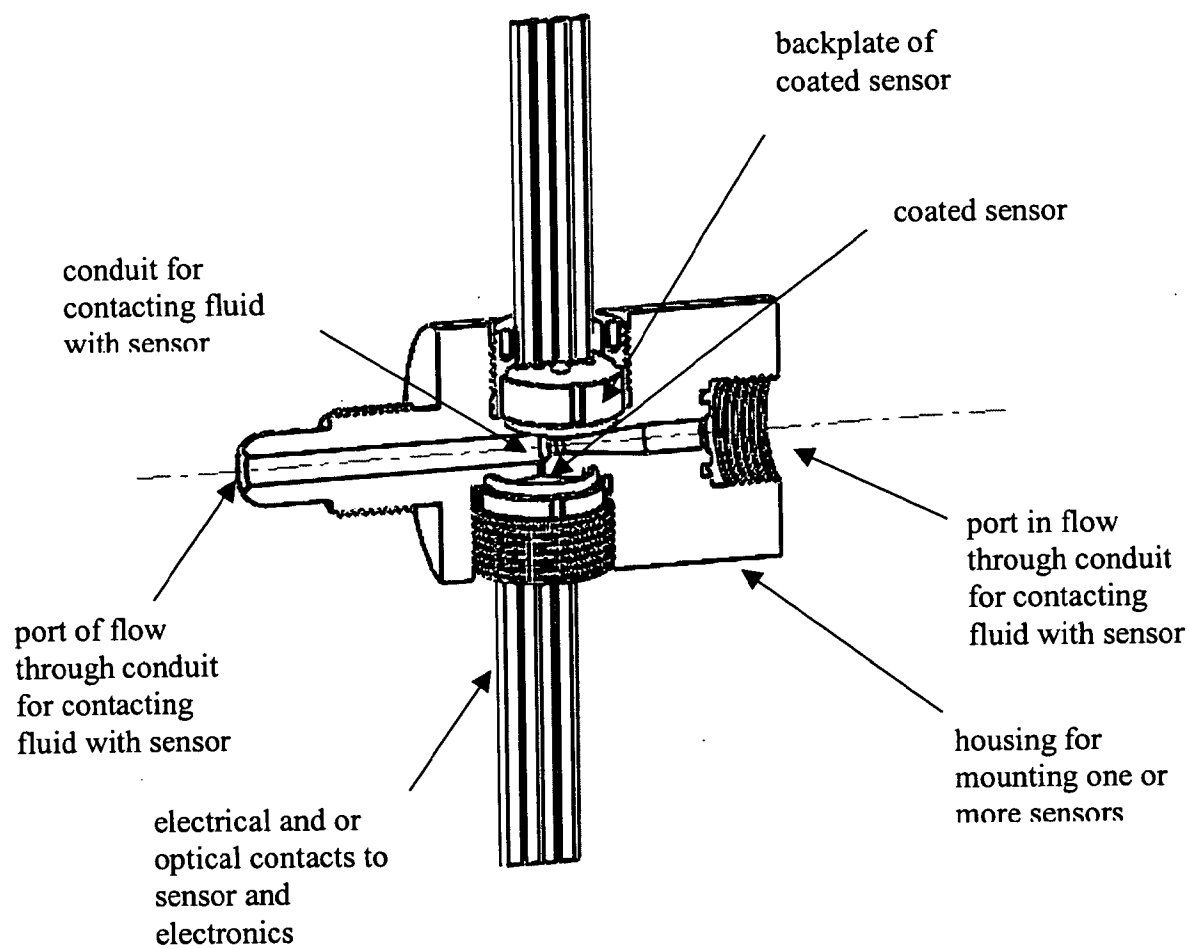


FIG. 5

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sensor surface to be contacted with  
a fluid whose property is to be  
measured, the sensor surface has an  
adherent non-porous coating of a  
poly-oligomer containing fluorine

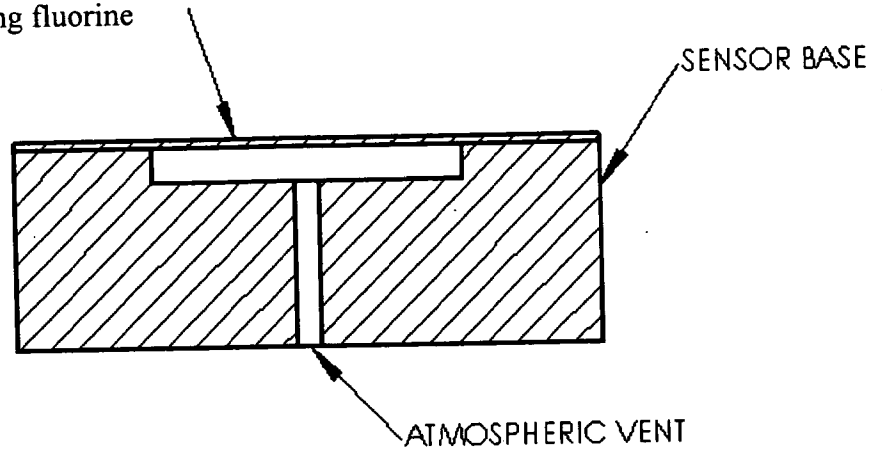


FIG. 6  
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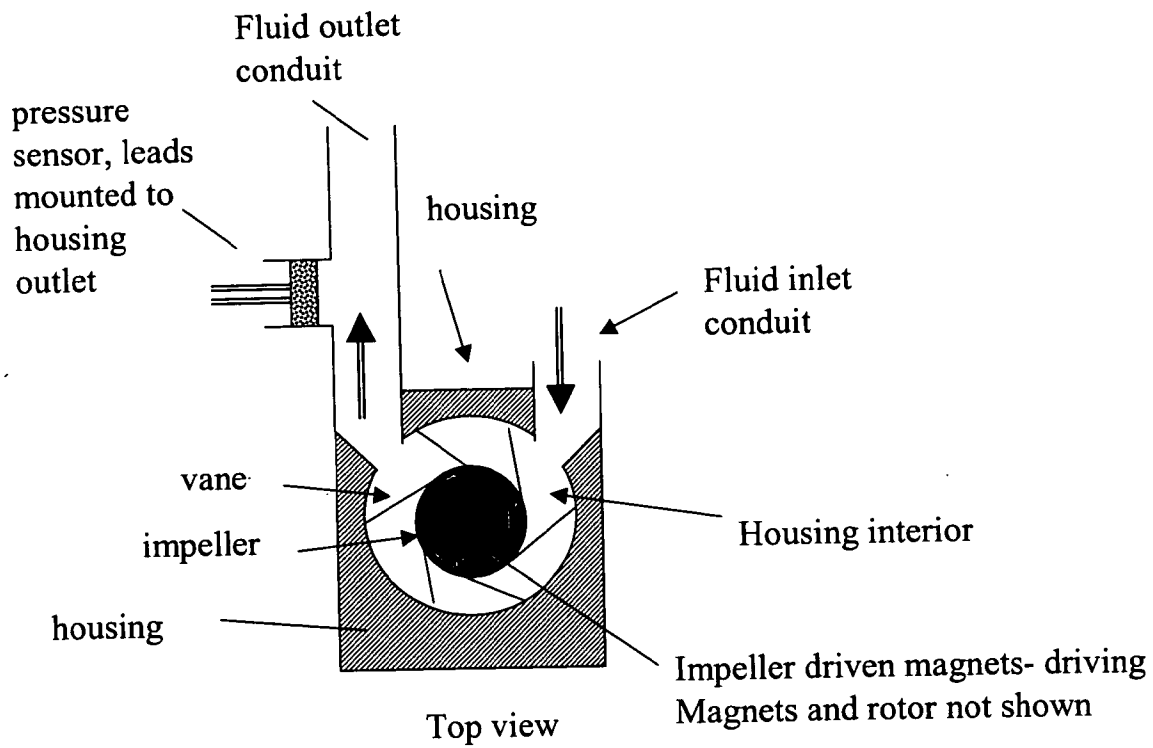


FIG. 7  
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APPLICATION DATA SHEET

APPLICATION INFORMATION:

Application Type:	Provisional
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Suggested Classifications:	
Suggested Group Art Unit:	
CD-ROM or CD-R:	
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